

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302 and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</p>			
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE <i>15 Aug 98</i>	3. REPORT TYPE AND DATES COVERED Reprint - July 1, 1994 to June 30, 1998	
4. TITLE AND SUBTITLE Tough Polymer Alloys via Chemically Controlled Morphology	5. FUNDING NUMBERS <i>DAAH04-94-G-0085</i>		
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemical Engineering Center for Polymer Research The University of Texas at Austin Austin, TX 78712-1062	8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>ARO 32510.33-CH</i>		
11. SUPPLEMENTARY NOTES The views, opinions and/or finding contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited		12b. DISTRIBUTION CODE	
12. ABSTRACT (Maximum 200 words) The use of functionalized polymers that react at the interfaces in polymer blends to form block or graft copolymers during melt processing has been examined. The graft copolymers function as "compatibilizers" that strengthen the interface and provide a powerful means of controlling blend phase morphology. Consequently, this approach provides an effective means of controlling the properties of multi-phase polymeric materials. Most of the work involved the use of polyamides, polyesters and polycarbonates as one component in the blend. The other component was a reactive elastomer, an ABS material, a core-shell impact modifier, or polypropylene. The end group configuration of the polyamide was shown to be an important consideration in morphology development. Functionalized additives are most efficient when both physical and chemical interacts are optimized. A variety of approaches for producing super-tough polyamide blends with low ductile-brittle transition temperatures are described. Cavitation of the rubber phase was shown to be an important part of the toughening mechanism in certain cases.			
14. SUBJECT TERMS			15. NUMBER OF PAGES 14
			16. PRICE CODE
16. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	17. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	18. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	19. LIMITATION OF ABSTRACT UL

Tough Polymer Alloys via Chemically Controlled Morphology

Final Report

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August 15, 1998

U.S. Army Research Office
Grant Number: DAAH - 04-94-G-0085

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I. STATEMENT OF PROBLEM STUDIED

Light-weight, super-tough materials may be formed by blending a rubbery phase (with appropriate morphology) into certain engineering thermoplastics; however, our understanding of how to control the morphology and its influence on toughness under extreme conditions (low temperatures, sharp notches, thick parts, ballistic rates of loading, chemical environments, etc.) is far from adequate. Furthermore, the limits on combining super-toughness with other desirable properties (high levels of stiffness, transparency, low permeability to chemicals, good processability, etc.) have not been extensively explored. To deal with these issues it is necessary to develop a thorough understanding of many issues and innovative strategies for solving key fundamental problems in the field of multicomponent polymer alloys (1-36). Our laboratory has a long term commitment to research that will supply these needed elements, and support of this program provides a rational and cost-effect approach to problem solving and materials development for both military and civilian applications.

When two polymers, A and B, are mixed, they in the extreme case form either a homogeneous, miscible mixture or one that is segregated into domains of essentially pure A and pure B depending on the thermodynamic interaction between the two polymers. Our program is unique in that it addresses both situations. We are interested in the quantification of the thermodynamic interaction energy between polymers A and B which is essential for identifying or molecularly designing miscible polymer pairs and controlling the mixture phase diagram (37-41). This interaction energy also governs the nature of the interface between the phases in immiscible blends which influences phase morphology and interfacial adhesion (45,46); elements that determine the degree of "compatibility" (see Figure 1). Our current ARO research and that proposed here is concerned with control of phase morphology and interfacial strength in phase separated blends. Our work on thermodynamics is funded by other sources, but the knowledge from that effort is essential in our ARO program for understanding the nature of the interfaces and for identifying functional polymers that have the necessary miscibility characteristics for reactive compatibilization.

$$\Delta G_{mix}/V = RT \left[\frac{\rho_A \phi_A}{M_A} \ln \phi_A + \frac{\rho_B \phi_B}{M_B} \ln \phi_B \right] + B \phi_A \phi_B$$

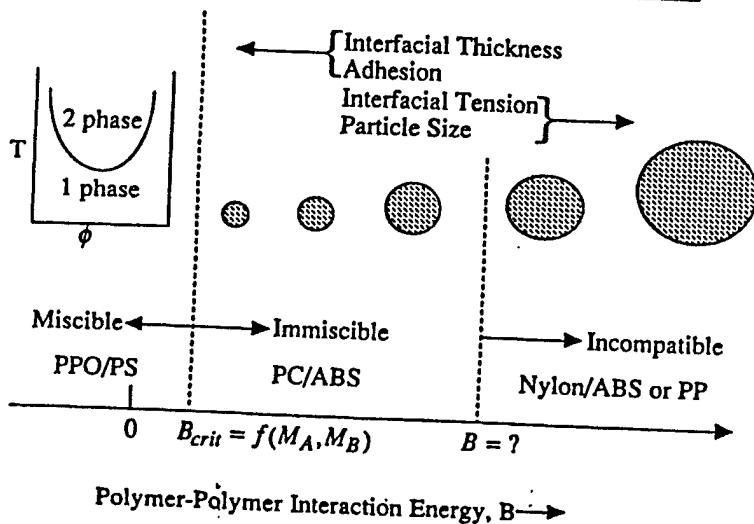


Fig. 1 Effect of polymer-polymer interaction energy (Flory-Huggins theory, see box) on blend compatibility

Most immiscible blends have poor mechanical properties relative to their components, and their phase morphology is strongly dependent on details of the processing history. The reason for this is the unfavorable interaction between molecular segments of the components, responsible for their immiscibility in the first place ($B > B_{critical}$), that leads to (a) a large interfacial tension in the melt which makes it difficult to properly disperse the components during mixing and drives phase rearrangements during low stress or quiescent conditions and (b) poor interfacial adhesion in the solid state which causes premature mechanical failure via these weak defects between phases. The severity of these problems depends on just how unfavorable the interaction energy is (see Figure 1). Remediation of these problems, or compatibilization, can be effected by the addition of appropriate block or graft copolymers that act as interfacial agents as demonstrated repeatedly over the last two decades (47). Grafting has

been widely used with considerable success to incorporate a rubber phase into brittle polymers to effect toughening (9, 28).

An attractive route is to form the block or graft copolymer *in situ* during blend preparation via interfacial reaction of added functionalized polymeric components (10, 48, 49). The functional groups, may be the reactive chain ends that occur naturally in condensation polymerization provided end capping techniques are not used. For addition polymers, functional groups can be placed along the chain by copolymerization or by grafting (e.g., maleic anhydride) (50-53) or at the chain end by special techniques (55-63). The functional groups may exist on all of the chains or only on some of them as discussed later. The functional groups to be used must be carefully selected such that adequate reaction can occur within the limited time frame of melt processing (a few minutes at most) where the only opportunity for encounter is at the interfacial region between the two polymer phases. In the following, we discuss several strategies for reactive compatibilization. Our program addresses the selection of the chemistry to be used (types of functional groups), synthesis to incorporate functional groups, processing, rheology, blend analysis (chemical and morphological), interfacial adhesion, mechanical properties and fracture characteristics of materials made by this method.

II. SUMMARY OF IMPORTANT RESULTS

In our last proposal submitted three years ago, we set goals of (a) introducing more sophisticated methods for evaluating toughness and for determining toughening mechanisms, (b) adding a twin screw extruder to our polymer processing laboratory to take advantage of the more intensive mixing such compounding devices offer, and (c) exploring new chemical schemes of reactive compatibilization. All of these have been implemented and the value of these techniques will become evident in the following subsections that describe research progress on topics related to the objective of this proposal. During the last three years, our laboratory has published or submitted a total of 34 papers in refereed journals based on research supported in full or in part by ARO (45, 46, 64-88).

1. Toughening of Nylon 6 with Reactive Elastomers

The most well-developed example of reactive coupling of phases in polymer blends is the rubber toughening of nylons (89-96) (see Figure 2). The most common route is the use of an ethylene/propylene type elastomer to which maleic anhydride has been grafted (at the level of 1 to 2% by weight), designated as EPR-g-MA, using well-known techniques. This material is melt blended with nylon where reaction of the anhydride unit with the nylon amine end groups occurs at the rubber-nylon interface to give grafted chains. This reaction can dramatically change the size of the dispersed rubber particles and the properties of the mixture. For nylon 6 and nylon 6,6, it seems to be well-established that the rubber particles must be within an optimum size range to generate super-tough materials (84, 97); however, there is a continuing debate about the fundamental reasons for the upper and lower limits on particle size.

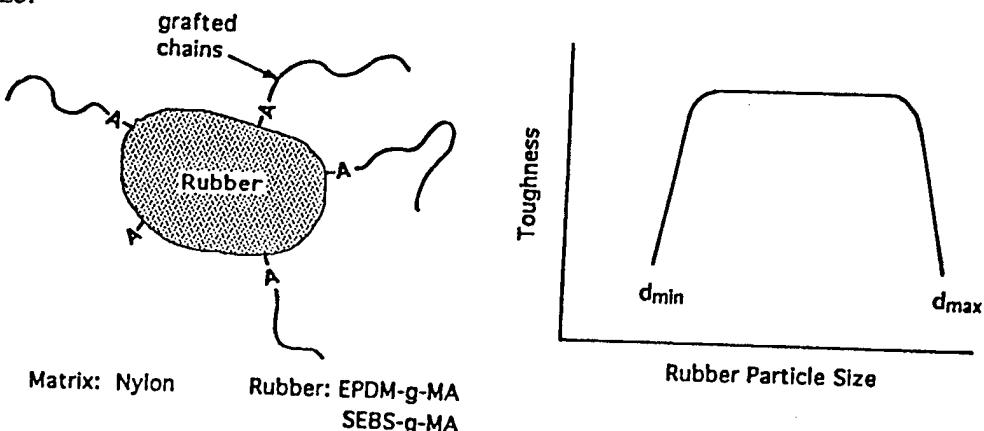


Fig. 2 Schematic illustration of toughening polyamides with reactive elastomers.

Our research in this area has also used a newly available styrene-based triblock copolymer that has maleic anhydride grafted to its ethylene/butene - like midblock (65, 77, 84-86, 97, 98). This material is designated as SEBS-g-MA while the unmaleated version is designated as SEBS. Blends of SEBS with either nylon 6 and nylon 6,6 lead to large rubber particles (~5 μ m in diameter) that do not adhere well to the polyamide matrix and there is no toughening. When SEBS-g-MA containing about 2% MA is blended in a single screw extruder with nylon 6 very small rubber particles of about 0.05 μ m are produced which can be too small for toughening (97). Similar blends with nylon 6,6 yield much larger particles of complex shape that are on the border of being too large for toughening; however, by

use of the more intensive shearing in a fully intermeshing, co-rotating, twin screw extruder these particles can be broken down to an optimal size for most effective toughening. The differences in reactive amine end group configurations of these materials is the cause for this behavior (97).

Recently we have completed comprehensive studies on how the type of rubber phase, the degree of maleation of the rubber phase, and the molecular weight of the nylon 6 matrix influences rubber particle size and the toughening of the blend (84, 85). Highlights from this work are briefly summarized here. For a medium molecular weight nylon 6, Figure 3 shows how the degree of maleation of the rubber affects its weight average particle diameter for three different rubber systems: SEBS-g-MA-X%

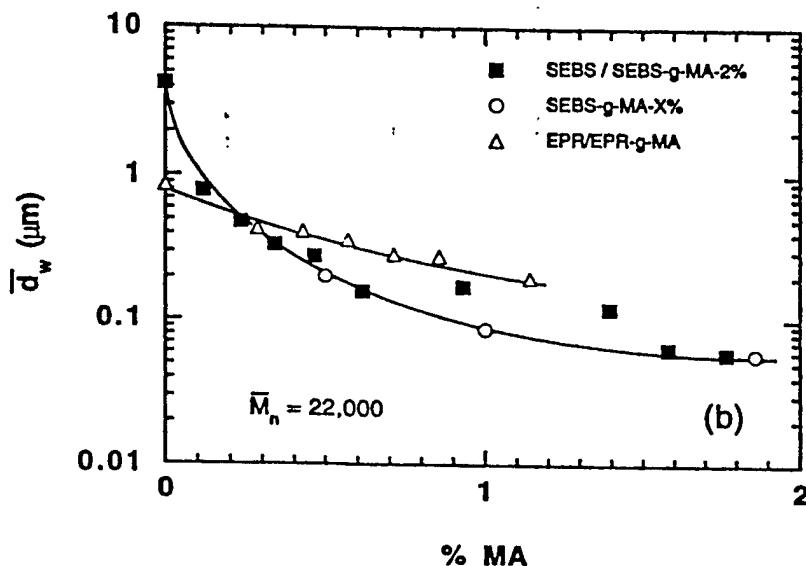


Fig. 3 Effect of maleic anhydride content in rubber on weight average rubber particle diameter for blends of SEBS/SEBS-g-MA-2%, SEBS-gMA-X%, and EPR/EPR-g-MA with nylon 6 ($\bar{M}_n = 22,000$), in the ratio 20% rubber/80% nylon 6.

where X% = the weight percent of maleic anhydride grafted to the SEBS precursor; mixtures of SEBS-g-MA-2% with the SEBS precursor, and mixtures of EPR-g-MA (degree of maleation = 1.14%) with the EPR precursor. As expected, the particles size decreases dramatically with increasing level of maleation; the trends are roughly the same for the two series of SEBS rubber systems but the EPR rubber system does not respond as strongly to maleation for reasons that will become more clear later. When compared at the same level of maleation, SEBS/SEB-g-MA mixtures produce particles that are slightly larger and which have a broader size distribution than SEBS-g-MA-X% materials as illustrated in Figure 4. However, the maleated/unmaleated rubber mixtures give a single population of particles similar in size to the uniformly maleated rubbers, which implies the two are miscible, and provides a useful tool for adjusting rubber particle size. For a given degree of maleation, rubber particle size

decreases as the molecular weight of the nylon 6 matrix increases, due mainly to the effects of the increased matrix viscosity during mixing in the extruder, as seen in Figure 5.

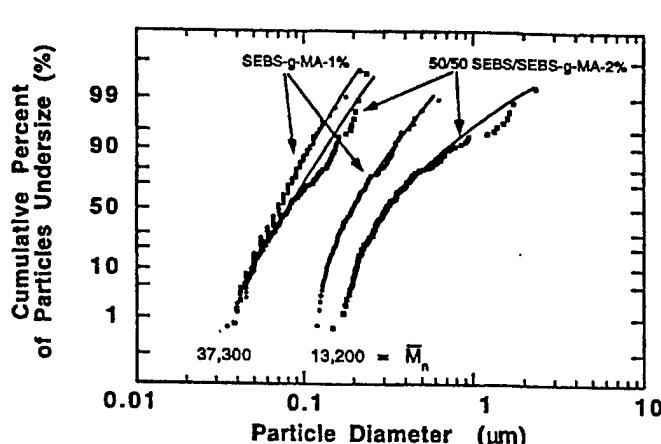


Fig. 4 Cumulative apparent particle size distributions for 20% SEBS-g-MA-1% and 20% 50/50 SEB/SEBS-g-MA% blends with 80% nylon 6 materials having number average molecular weights of 13,200 and 37,300. The two rubber systems being compared contain approximately 1% maleic anhydride by weight.

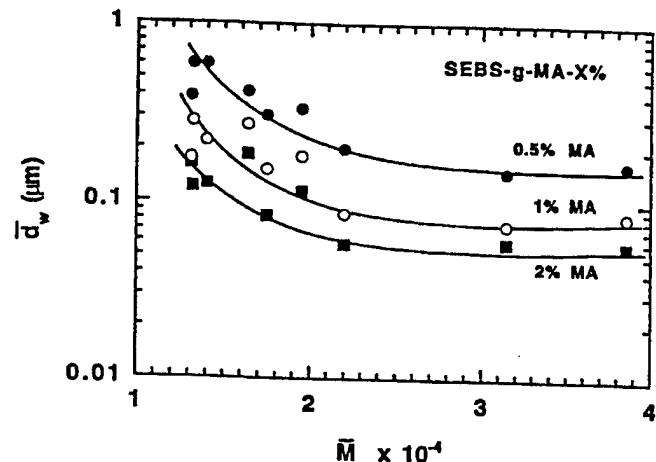


Fig. 5 Weight average rubber particle diameter of 20% SEBs-g-MA-X% 80% nylon 6 blends for X = 0.5%, 1%, and 2% as a function of nylon 6 molecular weight.

Figure 6 shows the upper and lower limits on rubber particle size for room temperature toughening (as defined schematically in Figure 2) determined as a function of the nylon 6 molecular weight. The range of sizes where super toughness is found gets broader the higher the polyamide molecular weight. The super tough size range is broader for the SEBS-based elastomers than the more limited data for EPR-based elastomers show. These limits for the SEBS system (Figure 6) are superimposed on the data for particle sizes generated (from Figure 5) in the composite plot shown in Figure 7. These results show for a fixed level of maleation that it is possible to generate super tough blends when the nylon 6 \bar{M}_n is low or high while intermediate values of \bar{M}_n do not lead to super tough blends. This unexpected behavior found earlier is now easily understood once the issues of morphology generation (Figure 5) and the particle size requirements (Figure 6) are rationally separated.

Other factors in addition to maleic anhydride content of the rubber phase influence the size of the rubber particles formed in blends with nylon 6, e.g., the relative and absolute rheological properties of the two phases, mixing intensity, and the extent of reaction which may be influenced by these and other factors. The molecular weight of the nylon 6 phase has been varied which influences the melt viscosity of the matrix and the number of amine groups available for reaction.

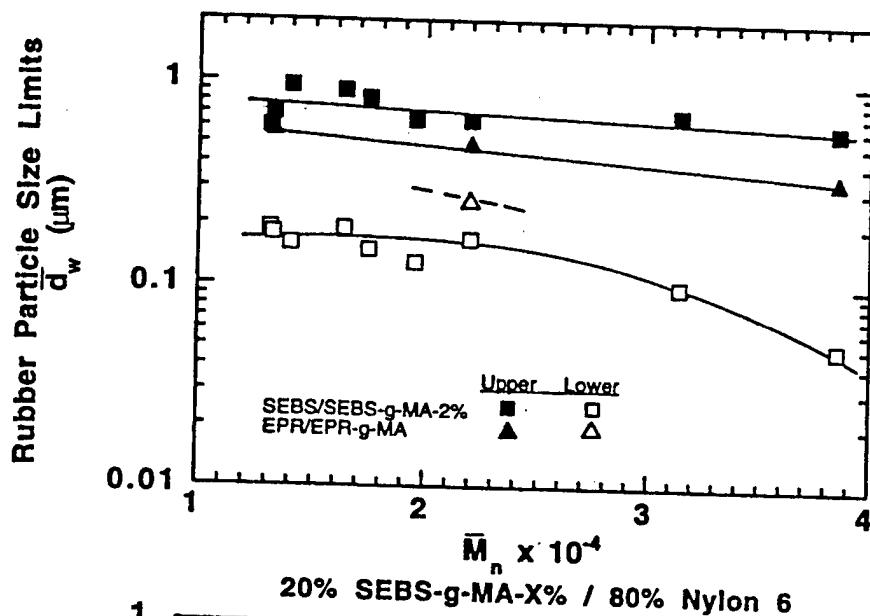


Fig. 6 Effect of nylon 6 molecular weight on the upper and lower rubber particle size limits for effective toughening of 20% SEBS/SEBS-g-MA2%/80% nylon 6 and 20% EPR/EPR-g-MA/80% nylon 6 blends.

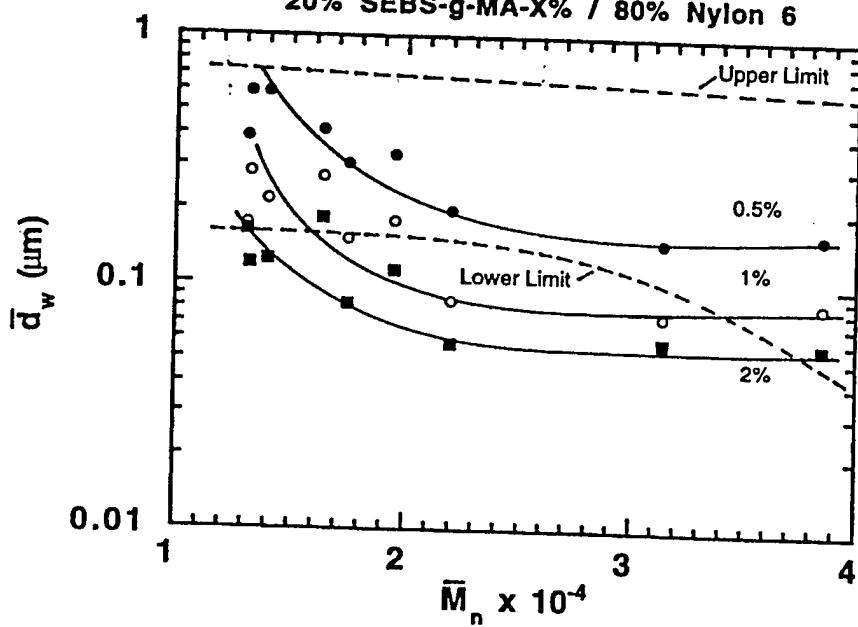


Fig. 7 The weight average rubber particle diameter of 20% SEBS-g-MA-X%/80% nylon 6 blends relative to the upper and lower size limits for effective toughening as a function of nylon 6 molecular weight and maleic anhydride content (X).

Based on many correlations published in the literature (99-104), the melt viscosity of the matrix phase should have an important effect on the size of the dispersed particles. This issue will be addressed later. The higher the molecular weight, of course, the fewer amine groups there are (see Figure 8a) to participate in grafting reactions; one might expect that the higher viscosity reduces the mobility needed to get the amine end groups to the interface. These factors may influence the amount of graft copolymer formed at the interface and ultimately the ability to disperse the maleated rubber in the nylon 6 matrix.

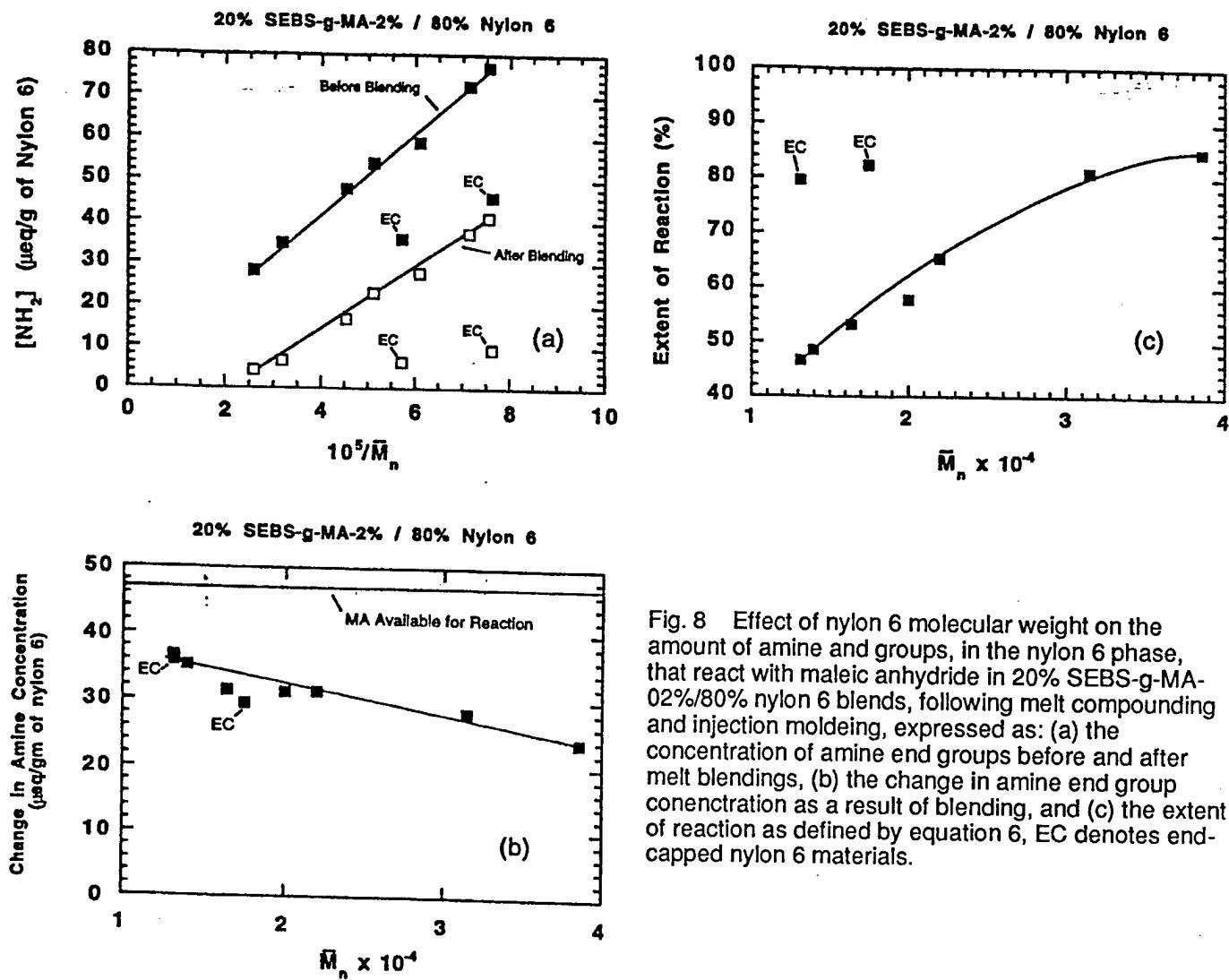


Fig. 8 Effect of nylon 6 molecular weight on the amount of amine and groups, in the nylon 6 phase, that react with maleic anhydride in 20% SEBS-g-MA-2%/80% nylon 6 blends, following melt compounding and injection molding, expressed as: (a) the concentration of amine end groups before and after melt blendings, (b) the change in amine end group concentration as a result of blending, and (c) the extent of reaction as defined by equation 6, EC denotes end-capped nylon 6 materials.

To characterize the amount of grafting that does occur, the amine concentration of the nylon 6 phase was measured by a titration technique before and after blending with 20% SEBS-g-MA-2%. The amine content prior to melt mixing increases linearly with the reciprocal of \bar{M}_n when there is one amine per chain, see the top line in Figure 8a; two nylon 6 materials fall below the line because of their reduced amine end content due to end capping (EC) during polymerization. The amine content after melt mixing and injection molding, the lower line in Figure 8a, follows a similar trend as the initial amine content except for a different slope. The unreacted amine concentration appears to approach zero for a value of \bar{M}_n of approximately 45,000 g/mol. The amine content before and after blending for the two end capped materials fall below the trend established by the polyamides having one amine end per chain by similar amounts. The difference between the two curves in Figure 8a indicates the absolute amount of

amine end groups that were consumed during the blending process if certain assumptions are made. The absolute amount of amine groups that react during blending decreases as the molecular weight of the nylon 6 increases as seen in Figure 8b. For all of these compositions, there are 47 μeq of maleic anhydride available for reaction per gram of nylon 6. Thus, there is an excess of amine groups relative to anhydride except for two of the highest molecular weight polyamides and the two end capped materials. The change in amine content as a result of blending for the two end capped nylon 6 materials falls in line with all the other materials when plotted versus molecular weight. Because there are fewer amine end groups available for reaction as the molecular weight of nylon 6 increases, it turns out that a larger fraction of the available amine groups reacts as the nylon 6 molecular weight increases as shown in Figure 8c. The extent of amine group reaction is defined here as

$$\text{Extent of amine reaction} = ([\text{NH}_2]_0 - [\text{NH}_2]_b) / [\text{NH}_2]_0 \times 100 \quad 1$$

where the subscripts 'o' refer to the initial amount and 'b' to the amount after compounding and molding.

In addition to the grafting caused by the reaction of amine end groups with maleic anhydride on the rubber to form imide linkages, other reactions may occur. However, the mixing times used here are short compared to those needed for the side reactions of hydrolysis or condensation to be significant as shown by Legras et al (105). On this basis, the loss of amine groups can be directly related to imide linkages or graft fraction. The extent of amine reaction is then the fraction of the nylon 6 chains that are grafted to the rubber phase, in the case of nylon 6 materials with one amine and one acid per chain. The two end capped nylon 6 materials have extremely high extents of reaction considering the reduced number of polymer chains that can participate in the reaction. However, as seen in Figure 8b, the absolute amount of amine groups that react in these materials is the same as for the non-end capped nylon 6 materials of equivalent molecular weight. The fact that the same number of grafted nylon chains are formed in each case helps explain why the end capped materials have nearly identical rubber particle size and distribution as the non-end capped nylon 6 materials. For the non-end capped nylon 6 materials, the fraction of polyamide chains grafted to the rubber phase increases monotonically as the nylon 6 molecular weight increases. The higher degree of grafting combined with the high melt viscosity, which generates greater stress on the rubber phase during dispersion, evidently results in smaller rubber particle sizes with lower polydispersity.

The morphology, or particle diameter d , of a two phase blend is the result of the balance between the processes of particle break-up and coalescence (106-108). Based on Taylor's theory for Newtonian fluids in a shear field, drop break-up will occur when the ratio of viscous to interfacial forces exceeds a critical value which is a function of the relative viscosities of the two phases. These principles have been used to describe dispersion phenomena that occur within flow fields for polymer blends.

Correlations of the following form have been developed:

$$\eta_m G d / \gamma = F(\eta_d / \eta_m) \quad 2$$

where γ is the interfacial tension, G is the shear rate, η_m the viscosity of the matrix phase and η_d the viscosity of the dispersed phase. The quantity on the left in equation 2 has been referred to as the capillary number (some references refer to this as the Weber number). Using models based on Smoluchowski's theory of aqueous colloid suspensions, attempts have been made to correlate the effects of coalescence on the size of particles formed (106, 109, 110). These theories predict that the dispersed phase particle size increases with concentration due to the greater probability of collisions as the number of particles increases (106, 111, 112). Reactions at the interface are expected to lead to a reduction in the interfacial tension, but their effect on stabilization against coalescence may be a more important consequence in blend morphology development (65, 106). Furthermore, such grafting reactions increase the viscosity of the mixture, or the level of stress when rotational speed of the mixing device is held constant, which tends to reduce particle size.

Numerous studies have attempted to unify data on particle size for various polymer systems, in the form suggested by equation 2, with some success. In non-reactive, immiscible polymer systems, a broad minimum in the capillary or Weber number has been observed for viscosity ratios between 0.1 and 1 (101-104, 107, 108). Wu has developed, for reactive and non-reactive rubbers melt blended with polyester and nylon 6,6 matrices, a master curve that shows a sharp minimum at a viscosity ratio of one (99). This implies that the smallest particles are formed, in reactive and non-reactive systems alike, when the viscosities of the matrix and dispersed phases are equal. For reactive systems, the viscosities refer presumably to those of the original components prior to any reaction. In what follows, we use the Brabender torque, T , at a fixed rpm to characterize the rheological properties of the pure rubber and pure

polyamide phases since more detailed rheological information is not available and the Brabender does provide a deformation field not unlike that in the extruder.

The current data can be unified in the form suggested by equation 2 with some modifications to the capillary or Weber number. All the blends in this study were prepared under identical conditions in a single screw extruder with a high intensity mixing screw. The stresses imposed on a dispersed phase within an extruder arise from a combination of complex shear and elongational flow fields. Thus, quantifying the intensity of mixing in an extruder is not so simple as estimating an effective shear rate since this is not a well-defined quantity, but in any case the kinematics of the mixing process used have been held constant here. Thus, for simplicity, we regard the shear rate in equation 2 as a constant. The interfacial surface tension is a difficult parameter to determine even for non-reactive systems and must be regarded as unknown for reactive systems. The interfacial tension will obviously vary according to the extent of reaction in the present blends. We deal with this factor by defining empirical shift factors as explained below. In consideration of the above issues, equation 2 can be transformed into the following:

$$(\alpha\beta)\bar{d}_w T_{\text{Nylon 6}} = F(T_{\text{Rubber}} / T_{\text{Nylon 6}}) \quad 3$$

where \bar{d}_w is the weight average rubber particle size, T_{Rubber} and $T_{\text{Nylon 6}}$ are the Brabender torque values of the rubber and nylon phase measured at 60 rpm and 240°C, and α and β are shift factors (defined more fully below) that account for the effective mixing intensity in the extruder, the interfacial surface tension of the blend system in the reacted state, increases in stress due to grafting reactions, and issues related to coalescence rate. An example of this modified Taylor theory analysis, prior to applying shift factors, is shown in Figure 9 for blends of the SEBS and SEBS-g-MA-X% elastomers with the various molecular weight nylon 6 materials. It is apparent that each curve has a similar shape and slope; i.e., the curves are merely vertically displaced from one another to an extent that reflects the amount of maleic anhydride in the rubber. Thus, a master curve can be generated by selecting a reference curve and shifting the other curves to this reference.

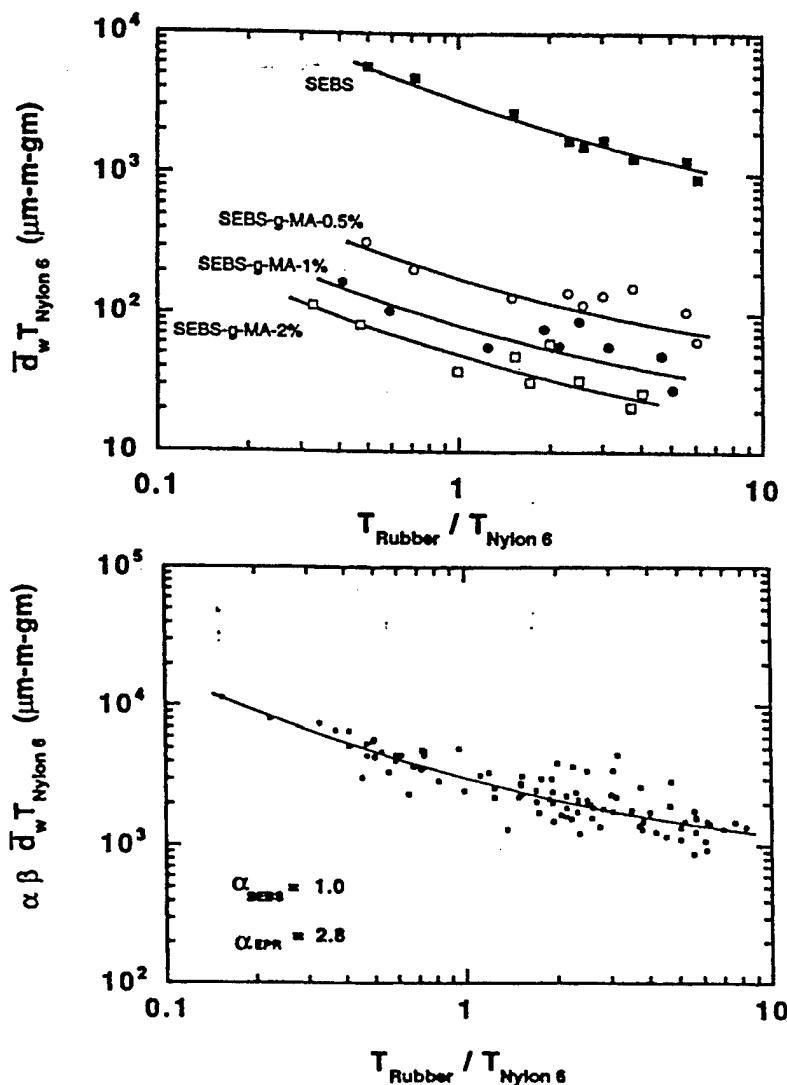


Fig. 9 Modified capillary or Weber number analysis for 20% SEBS-g-MA-X%/80% nylon 6 blends as a function of the melt viscosity ratio for the rubber phase to the nylon 6 phase. Melt viscosity determined from Brabender torque response after 10 minutes at 240°C and 60 rpm.

Fig. 10 Modified capillary or Weber number analysis master curve using shift factors to effect superposition of the maleated rubber curves on the non-maleated reference curve, SEBS.

The non-maleated SEBS curve was chosen as the reference, and the curve for each maleated rubber was shifted until it coincided with the SEBS reference curve. The magnitude of this shift on a logarithmic scale defines the multiplier or overall shift factor, $\alpha\beta$, required to achieve vertical superposition. The overall shift factor can be further divided into shift factors corresponding to the rubber type, α , and the maleic anhydride content in the rubber phase, β . That is, β is the value for shifting a maleated rubber curve to its non-maleated counterpart, SEBS or EPR. For example, multiplying each data point on the SEBS-g-MA-2% curve by the appropriate factor, $\beta = 65$, gives superposition onto the SEBS curve. The factor α , associated with the rubber type, allows the EPR/EPR-g-MA rubber system to be shifted to the SEBS reference curve. Multiplying the data points on the EPR curve by $\alpha_{EPR} = 2.8$ provides the best superposition onto the SEBS curve. The values of α_{SEBS} and β_{SEBS} are unity since the SEBS curve has

been chosen as the reference. For L-SEBS-g-MA (this block copolymer has a low amount of styrene or short end blocks relative to SEBS), only the overall shift factor, $\alpha\beta$, could be determined since no non-maleated precursor was available for this study.

This procedure, using SEBS as the reference, leads to the master curve shown in Figure 13. There appears to be good correlation among the data suggesting that a unification of the rubber particle size influenced by the numerous chemical and physical parameters is possible. It is evident that there is no minimum at a viscosity ratio of unity as suggested by Wu (99), even for the non-maleated rubbers, SEBS and EPR. The overall shift factor, $\alpha\beta$, in equation 3 physically represents a combination of the shear rate (a constant), the interfacial surface tension and any factors not explicitly considered in the theory (equation 2) such as changes in the coalescence process. The interfacial tension and coalescence rate are expected to decrease as the amount of grafting of the nylon 6 to the rubber phase increases with maleic anhydride content. Therefore, the overall shift factor should be a strongly increasing function of the maleic anhydride content of the rubber as shown in Figure 11.

Each rubber system shows a remarkable linear correlation between the overall shift factor and the maleic anhydride content. The larger the shift factor the smaller the rubber particles. Thus, the large shift factors for SEBS-g-MA-X% materials lead to the smallest rubber particle sizes due to their efficiency to react and reduce the interfacial tension and coalescence rate. The effect of the viscosity ratio on the Weber number relative to nylon 6 molecular weight appears to be constant since the slopes of all the curves are nearly identical. The data scatter at high viscosity ratios, i.e., the low molecular weight nylon 6 materials at low maleic anhydride contents, may suggest that the grafting reaction is not enough to reduce the rubber particle size and that viscosity effects are still important in morphology generation.

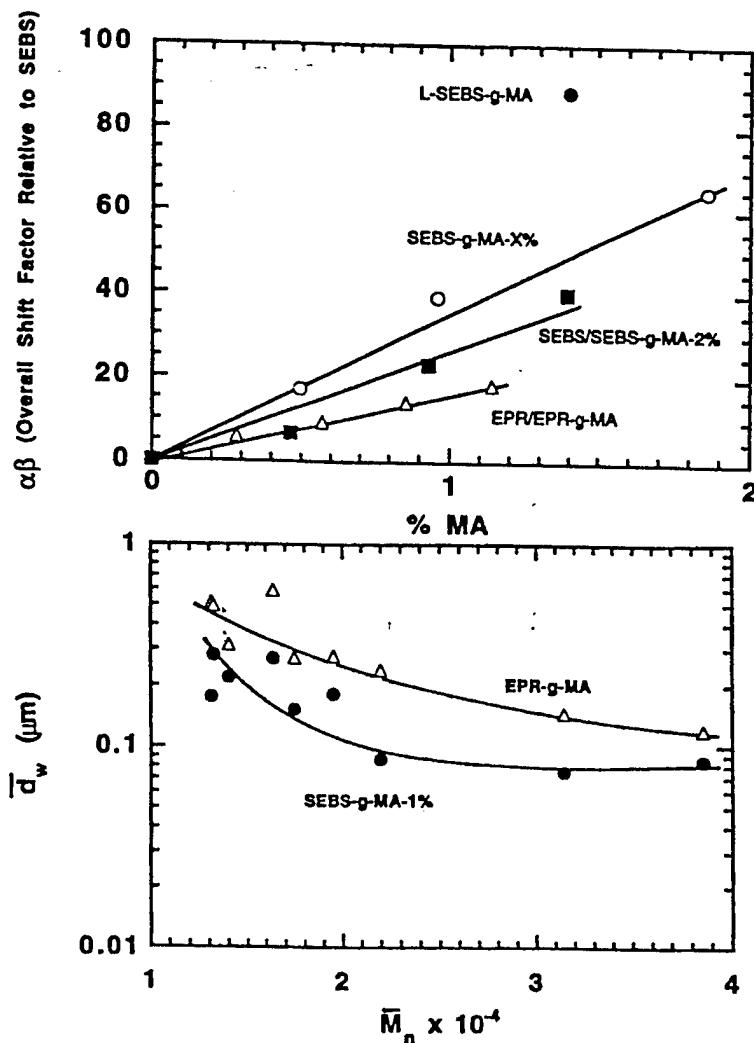


Fig. 11 Overall shift factors for 20% rubber/80% nylon 6 blends as a function of maleic anhydride content.

Fig. 12 Effect of nylon 6 molecular weight on weight average rubber particle diameter for blends of 20% SEBS-g-MA-1%/80% nylon 6 and 20% EPR-g-MA/80% nylon 6. Note that both rubbers contain approximately 1% maleic anhydride by weight.

It is apparent from Figure 11 that the EPR and SEBS-based elastomers have different shift factors. A direct comparison of rubber particle sizes for the two rubber types is shown in Figure 12 as a function of the polyamide molecular weight. The rubber particles are larger for EPR-g-MA than SEBS-g-MA-1%, even though the former has a slightly higher maleic anhydride content than the latter, regardless of the nylon 6 molecular weight. Torque rheometry has frequently been used to monitor chemical reaction during reactive melt mixing (92, 97). Figure 13a shows the Brabender torque responses of SEBS and EPR type rubbers of similar melt viscosities and levels of maleation. However, when blended with nylon 6, the SEBS-g-MA-1% leads to a significantly greater torque value than EPR-g-MA, as seen in Figure 13b, suggesting a greater level of reactive grafting to the former than the latter.

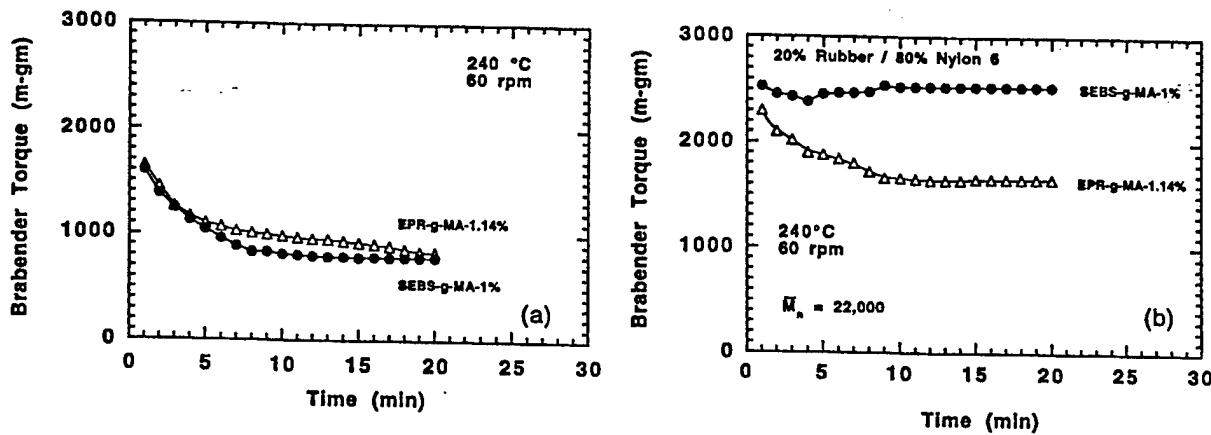


Fig. 13 Brabender torque response (at 240°C and 60 rpm) for (a) EPR-g-MA and SEBS-g-MA1% and (b) of EPR-g-MA and SEBS-g-MA-1% blends with nylon 6 having $\bar{M}_n = 22,000$ in the ratio 20% rubber/80% nylon 6.

The proposed difference in reactivity between the two maleated rubber types was confirmed by using the titration technique mentioned earlier (113). Figure 14 shows that the extent of reaction of the SEBS/SEBS-g-MA-2% and SEBS-g-MA-X% materials with a medium molecular weight nylon 6 increases monotonically as the amount of maleic anhydride in the rubber phase increases; however, the

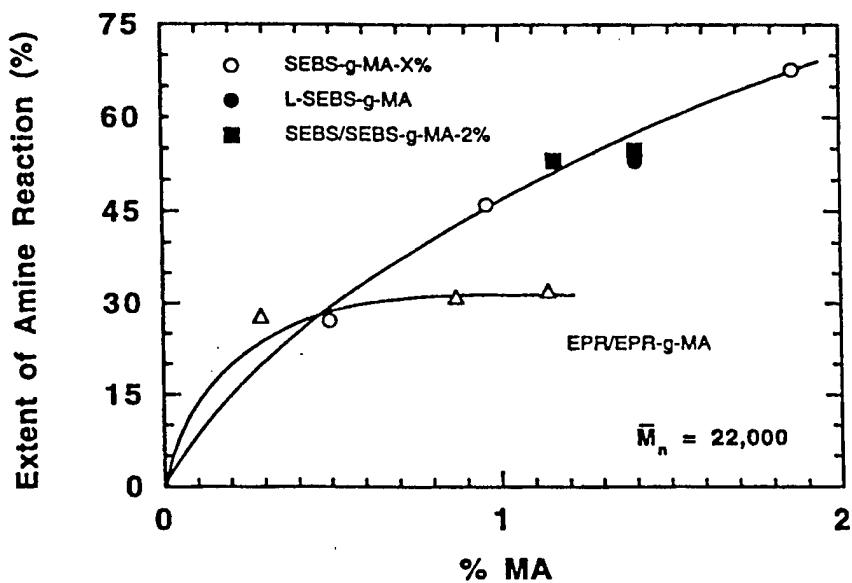


Fig. 14 Effect of maleic anhydride content of the rubber phase on the extent of amine reaction in 20% rubber/80% nylon 6 ($\bar{M}_n = 22,000$) blends, for the rubbers EPR/EPR-g-MA, SEBS/SEBS-g-MA-2%, SES-g-MA-X%, and L-SEBS-g-MA, following melt compounding and injection molding.

EPR/EPR-g-MA mixture apparently shows a greater extent of reaction at low maleic anhydride levels and then does not change at higher levels of maleic anhydride. A similar trend was observed in the power, or electrical current readings, needed to operate the extruder at a fixed rpm (113). Figure 14 clearly shows that highly maleated SEBS elastomers react to a greater extent with this nylon 6 and are, therefore, more likely to produce smaller rubber particles than EPR/EPR-g-MA elastomer mixtures. The

reason for this difference in reactivity must be the result of some structural differences between the two rubber types, but at this point we can only speculate on what these differences may be.

Most of the literature on rubber toughening focuses on the fracture behavior at room temperature only; however, demanding applications require that toughness be maintained to low temperatures. Super tough plastics exhibit a transition from ductile to brittle behavior as the temperature is reduced; this is illustrated in Figure 15 for blends of nylon 6 with mixtures of EPR/EPR-g-MA. The ductile-brittle transition occurs at lower temperatures the more EPR-g-MA in the rubber phase mixture. This is because the rubber particle size decreases with increased levels of maleic anhydride in the rubber (see Figure 3) and the ductile-brittle transition temperature is reduced to lower levels the smaller the rubber

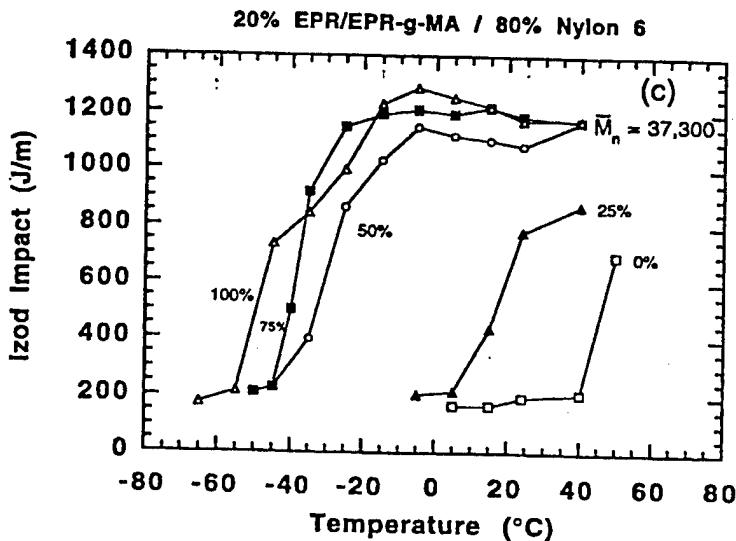


Fig. 15 Effect of rubber phase maleic anhydride content on Izod impact strength versus temperature for blends of EPR/EPR-g-MA with nylon 6 in the ratio of 20% rubber/80% nylon 6. Data are shown here only for selected rubber mixtures. For nylon 6 matrix, $M_n = 37,300$.

particle size, see Figure 16, at least to a certain limit. For SEBS-g-MA materials, very small rubber particles cause the ductile-brittle transition temperature to reverse direction and rise above room temperature. As shown earlier, at a given level of maleation EPR-based rubber particles are larger than those formed from SEBS-based rubber; in spite of this, the ductile-brittle transition temperatures for the blend with the former are considerably lower than those with the latter for all nylon 6 molecular weights as shown in Figure 17.

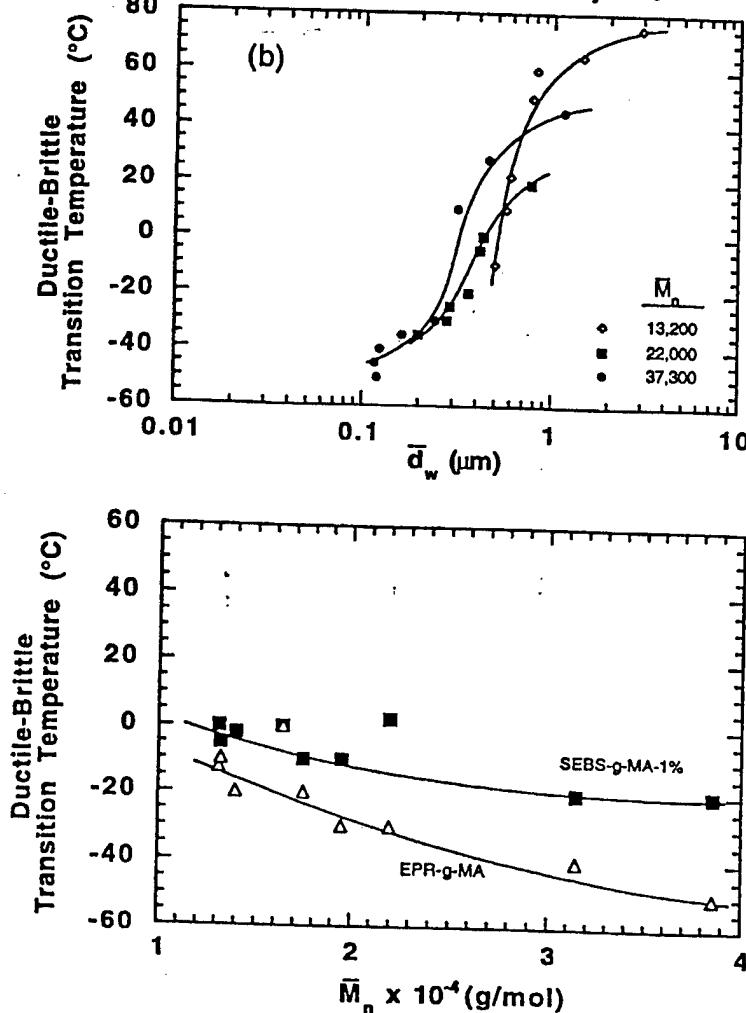


Fig. 16 Effect of weight average rubber particle diameter on the ductile-brittle transition temperature for blends of 20% rubber/80% nylon 6 ($\bar{M}_n = 13,200, 22,000$, and $37,300$) with EPR/EPR-g-MA mixtures.

Figure 17 Effect of nylon 6 molecular weight on the ductile-brittle transition temperature for blends with 20% SEBS-g-MA-1% and 20% EPR-g-MA. These two elastomers have similar maleic anhydride contents.

The better low temperature toughness achieved by blending with EPR-based rubber is related to the lower modulus of this material at low temperatures compared to SEBS-based materials which are more rigid owing to the hard styrene-segment microdomains that reinforce and "crosslink" these block copolymers. This is illustrated in Figure 18 where the ratio of the nylon 6 modulus to that of several rubber systems is shown as a function of temperature. The modulus ratio is a factor in classical theories that explain toughening mechanisms in terms of stress-concentration in the matrix caused by soft rubber particles (114-119). In fact, the rule of thumb that the rubber should have a modulus one tenth of that of the matrix for toughening (118, 119) occurs at a temperature approximately equal to the lowest ductile-brittle transition temperatures found for blends based on EPR and SEBS-type rubbers. However, the recent literature provides considerable evidence that the simple notion of stress concentration is not adequate to explain the role of rubber particles in the toughening of semi-ductile matrices (116). In fact,

these is evidence that a main role of the rubber particle is to cavitate under conditions of triaxial stress thereby relieving this state of stress and allowing the matrix to shear yield (116, 117, 120). Work from this laboratory supports the latter view (69, 77, 86). It is interesting then to compare the propensity of EPR and SEBS rubber particles to cavitate.

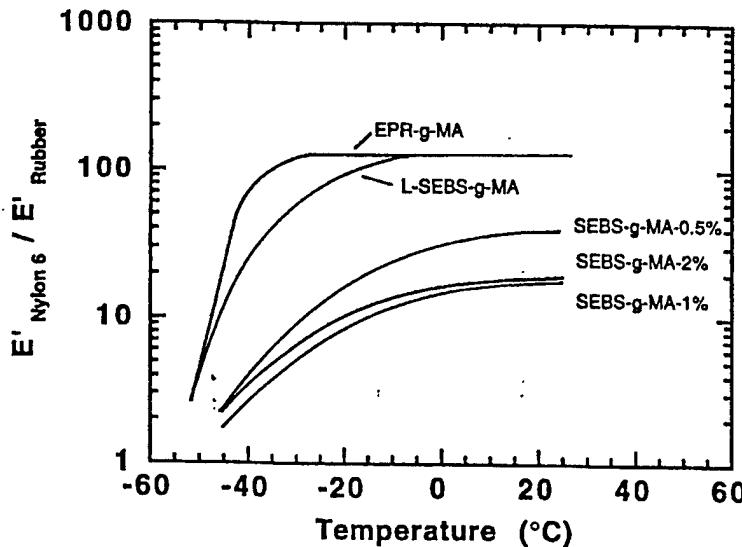


Fig. 18 Matrix to rubber modulus ratio as a function of temperature for the rubbers SEBS-g-MA-X%, L-SEBS-g-MA and EPR-g-MA.

Figure 19 compares low speed tensile stress-strain diagrams for nylon 6 blends with these two types of rubber. Also shown are volume strains measured simultaneous during this test by a volume dilatometer (77). The EPR-based blend shows considerable post-yield dilation whereas the SEBS-based blend shows no post-yield dilation. Post-mortem microscopy indicates that the EPR particles cavitated

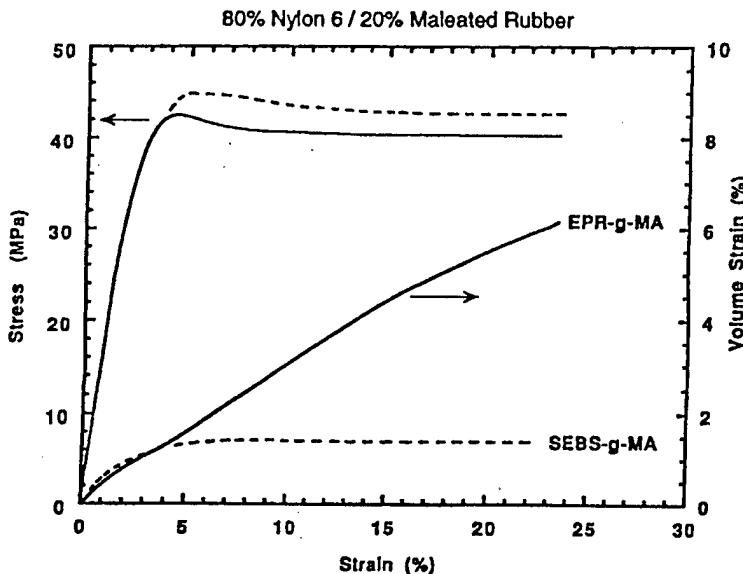


Fig. 19 Stress and volume strain versus tensile strain for two super tough nylon 6 compositions.

while the SEBS particles did not. Post-mortem microscopy of specimens with arrested impact fractures reveals that SEBS particles can cavitate, but they apparently only do so under severe conditions of

triaxial stress (77). This evidently is a result of the micromechanical properties of this elastomer which stems from the effects of its hard block microdomains. Further work related to the cavitation characteristics of the rubber phase may be very fruitful.

The schematic to the right of Figure 20 summarizes an extensive transmission electron microscopy examination of sub-critically fractured super tough nylon 6 materials (86). There is a zone around the crack tip where the matrix has undergone extensive shear yielding; beyond that is a zone where the rubber particles are cavitated. In the shear zone the cavities that were formed in the rubber particles have collapsed. The size of the deformed zone was measured for a series of super tough materials, and it appears that there is a unique correlation of fracture energy with the size of this deformed zone as seen in Figure 20 for a number of materials. This suggests that the main mechanisms of energy absorption is plastic deformation of the nylon 6 matrix and that impact energy absorption per unit volume of deformed material is a constant. Factors related to the rubber properties or morphology simply act to control the size of the deformed zone. Control of the deformed zone size appears to be the key to super toughness.

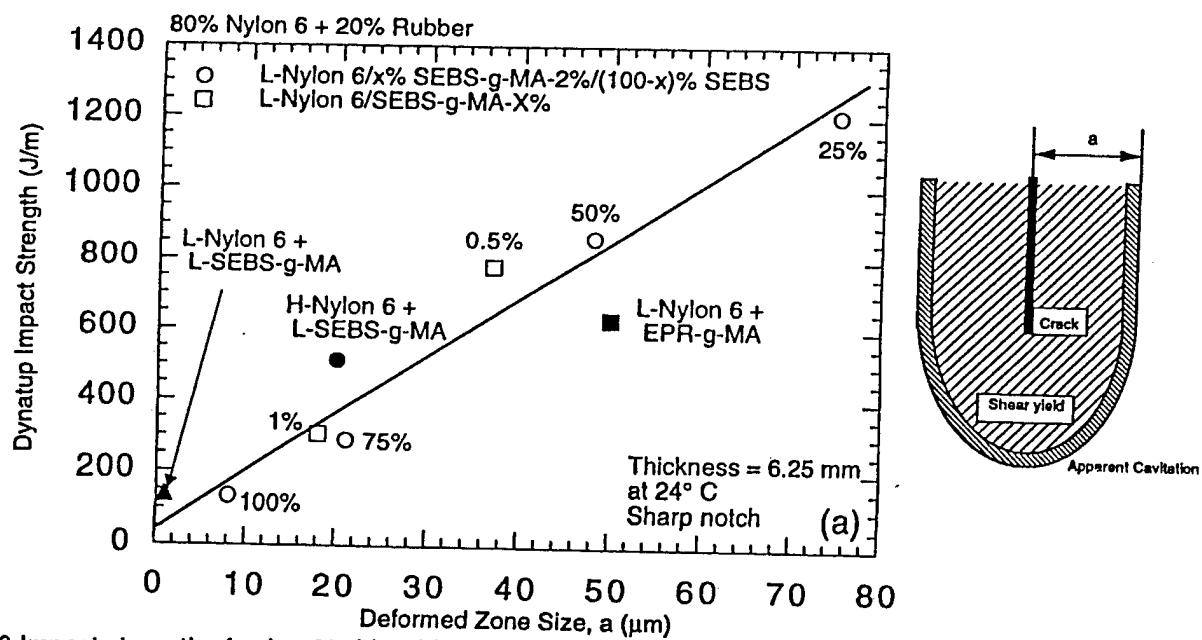


Fig. 20 Impact strength of nylon 6/rubber blends as a function of deformed zone size (an schematic to the right) measured by transmission electron microscopy.

Most of the literature, as well as our own work, has relied on the use of the standard notched Izod impact test or similar procedures to characterize the toughness of these blends. These methods have been used because of convenience and their general use in the plastics industry. They allow easy

comparison with other systems; however, the fracture energies obtained by these tests are certainly not material constants and provide only a limited picture of how the material responds to stress in the presence of a crack.

More sophisticated test methods based on fracture mechanics offer means to better characterize the toughness and to understand the deformation mechanisms that occur in toughened engineering thermoplastics (121-133). However, techniques based on linear elastic fracture mechanics (LEFM) are not fully appropriate for such pseudo-ductile materials. Furthermore, determination of the classical critical stress intensity factor (K_{IC}) requires testing of very thick specimens of materials having low yield strength and high toughness like rubber toughened blends in order to satisfy the small scale yield criterion (133). Such thick specimens cannot be formed easily by injection molding which is a preferred method for fabricating plastic parts. For these reasons, the J-contour integral method has been recently regarded as more appropriate for such polymeric materials and has the benefit of not requiring exceedingly thick specimens (133). However, the thickness required is still often beyond what can be conveniently injection molded. Rigorous measurement of J_{IC} involves use of rather specialized equipment and techniques.

A technique recently proposed by Vu-Khanh (125) offers an approach for characterizing fracture that is a useful compromise between rigorous fracture mechanics methodology and the simplicity of Izod or Charpy measurements. In this method, the energy required to fracture a specimen, U , with a ligament area, A , is measured by a standard or instrumented impact tester. It has the advantage of high test speeds corresponding to impact conditions as opposed to essentially static loading conditions usually employed in J_{IC} measurements. Considerably greater insight about the fracture toughness of ductile plastics can be gained from analysis of the fracture energy as a function of the ligament area (121, 125). Vu-Khanh showed that the fracture energy per unit of ligament area, U/A , is a linear function of the ligament area A and defined the two parameters in the relationship

$$\frac{U}{A} = G_i + \frac{1}{2} T_a A \quad (2)$$

Thus, this analysis yields a fracture energy at initiation, G_i , and a measure of the additional energy associated with propagating the fracture, or tearing modulus, T_a . Vu-Khanh has claimed that the fracture energy at initiation, G_i , is equivalent to the critical J-integral for fracture, J_{IC} . Mai (134) pointed

out that the Vu-Khanh approach is equivalent to the essential work analysis proposed by Mai, Williams, et al (124, 135-137) and have questioned equating G_i to J_{IC} . Regardless of the interpretation used, this approach provides considerable useful information about the fracture process that goes well beyond the Izod or Charpy tests, both of which may be regarded as single point methods (one value of A) in this context.

This technique has been used to characterize the fracture toughness of blends of nylon 6 with SEBS-g-MA-2% + SEBS and SEBS-g-MA-X% rubbers. The fracture energy at initiation and tearing modulus plus the size of the deformed zone (as determined by TEM analysis) increase as the rubber particles become larger; however, the relationships for the two rubber series are different as shown in Figure 21. The total fracture energy seems to be uniquely related to the size of the deformed zone as

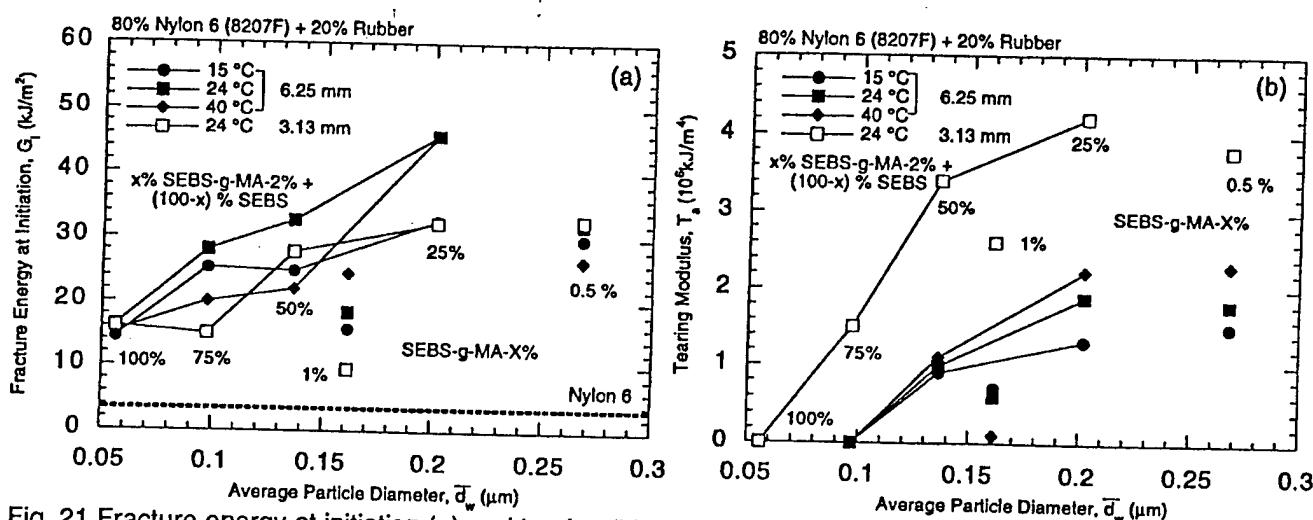


Fig. 21 Fracture energy at initiation (a) and tearing (b) as a function of a average rubber particle diameter.

shown above. The onset of super-tough behavior appears to be related to the emergence of finite values of the tearing modulus. Such materials show ductile fracture under plain strain conditions caused by either thick specimens or sharp notches. Toughening is caused by shear yielding of the nylon 6 matrix which is evidently triggered by rubber particle cavitation. Blends containing very small rubber particles (ca 50 nm) are not tough, and such particles show very little cavitation during fracture.

2. Reactive Dispersion of Core-Shell Impact Modifiers in Polyamide Matrices

Emulsion polymerization is used to make core-shell type impact modifiers for toughening rigid but brittle or notch-sensitive polymers (9, 28). Such modifiers are especially convenient because particle size can be precisely set independently of processing and rheological parameters. The core of the particle contains the elastomer while the shell functions to aid dispersion in the matrix and to couple the particle to the matrix among other things. Usually the shell-matrix interaction is physical, i.e., the grafted chains are identical with the matrix or is miscible with it, e.g., PMMA or SAN grafts for PVC toughening. Such compatibility or miscibility usually does not exist between matrices consisting of engineering polymers, like nylons, polyesters, polyacrylates, etc., and the types of polymers that can be used as the shell material. One means of solving this coupling problem is to incorporate functional units into the shell material by copolymerization; however, we have developed a useful and simpler alternative.

We have shown previously that styrene/maleic anhydride (SMA) copolymers, over a certain range of MA comonomer content, are miscible with PMMA (138, 139). Of course, the anhydride groups can react with polyamides. Thus, we proposed that small amounts of SMA can be used to disperse conventional impact modifiers (with PMMA grafted shells) in polyamides, an extensive study recently completed in our laboratory and now published have demonstrated the effectiveness of this idea (64, 75, 140). In addition, a theoretical thermodynamic model has been developed (78) for the solubilization of the functional polymer in the restricted space of the grafted chains that form the shell of the impact modifier. Another paper (79) published recently documents experimental evidence of the solubilization predicted by the model.

3. Nylon 6/Polypropylene Blends

There has been considerable commercial interest in blends of polyamides with polyolefins driven by the need to reduce the water sensitivity of nylon and the cost of these materials. To achieve compatibilization, polyolefins have been functionalized, primarily by grafting of maleic anhydride, for

reaction with the nylon component. While this approach is commercially useful, very few detailed investigations concerning morphology generation and properties had appeared when we initiated the work described below (74, 77).

Blends of nylon 6 and polypropylene materials (regardless of interfacial bonding or morphology) are not very tough since neither component is tough (see Figure 22). Addition of rubber is needed to achieve toughening of these blends. Figure 23 shows the room temperature Izod impact strength for nylon 6/PP blends containing 20% of either SEBS-g-MA or EPR-g-MA containing approximately 1% MA. Figure 24 shows how impact strength varies with temperature for a fixed PP content but a varying amount of EPR-g-MA. These results show that materials can be achieved which are supertough at room temperature and that have remarkably low ductile-brittle transition temperatures.

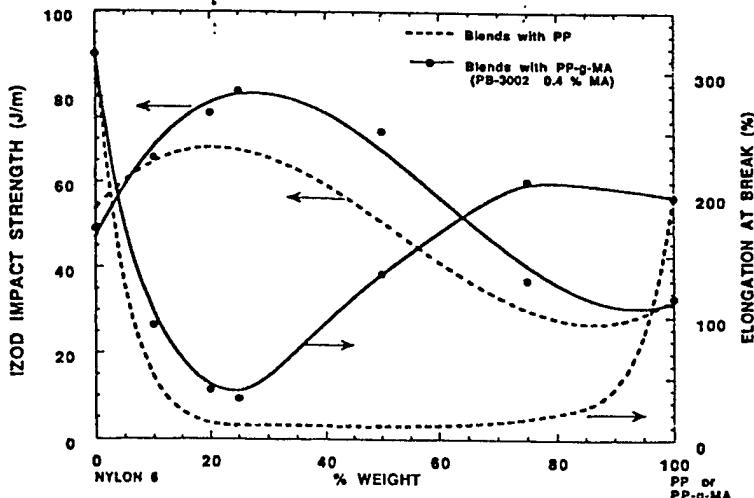


Fig. 22 Room temperature Izod impact strength and elongation at break for binary blends of nylon 6 and polypropylene (dashed line) or maleated polypropylene (solid line).

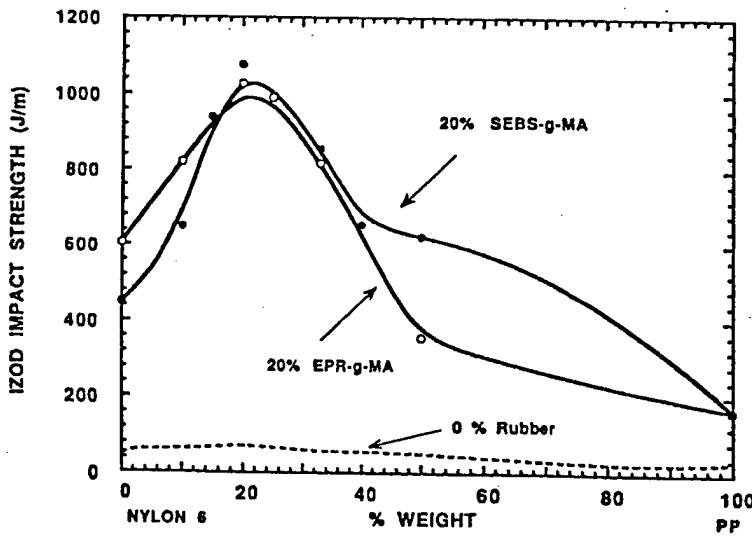


Fig. 23 Room temperature impact strength of rubber toughened nylon 6/PP blends.

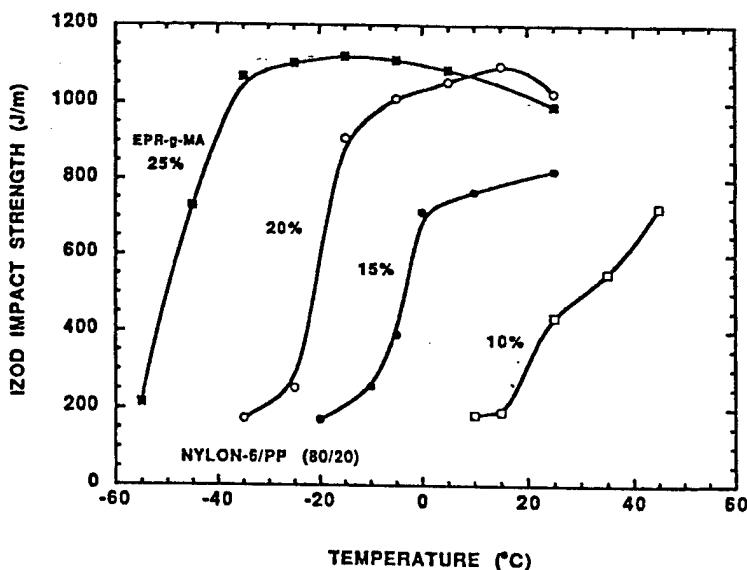


Fig. 24 Effect of temperature on the Izod impact strength of 80/20 nylon 6/PP blends modified with different amounts of EPR-g-MA.

The morphology of nylon 6/PP blends with the two maleated rubbers, as revealed by extensive TEM observations, is conveniently summarized by the schematics shown in Figure 25. Binary blends of the different components of the rubber-modified blends have similar morphologies; a dispersed phase of one component in a matrix of the remaining component. Which phase is the matrix and the size of the dispersed phase depends on the volume and viscosity ratios of the components. The rubber domains in the nylon 6/maleated rubber blends are usually very small due to the reaction that takes place between these two polymers during melt processing. In contrast, TEM photomicrographs of ternary blends of nylon 6, polypropylene, and the maleated rubbers reveal a quite different type of morphology; some of the rubber tends to be dispersed in the nylon 6 phase while the remainder tends to locate at the interface between nylon 6 and polypropylene. That is, the rubber seems to act as an impact modifier for the nylon 6 phase and also as an interfacial compatibilizer for the blend. At a fixed weight fraction of rubber, the relative size of the polypropylene domains is a function of both its volume fraction and its viscosity. At a certain composition phase inversion takes place and the polypropylene becomes the continuous phase. However, the location of the rubbery phase does not seem to change with these gross changes of morphology.

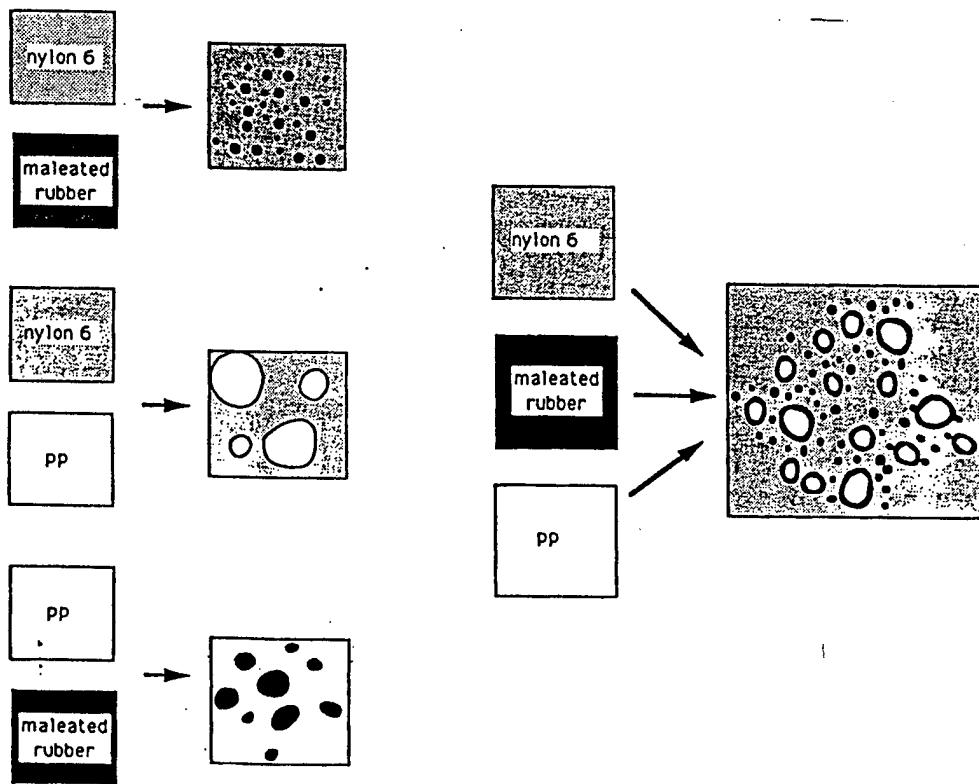


Fig. 25 Schematic of the morphology of binary and ternary blends of maleated rubber, nylon 6 and polypropylene.

Figure 26 summarizes the response of the ductile-brittle transition temperature of blends containing 20% EPR-g-MA (1.14% MA) as a function of the PP-g-MA content of in the blend. The solid lines indicate blends based on PP-g-MA materials, while the dashed line is for blends based on unmaleated PP. Up to 16% PP-g-MA the ductile-brittle transition temperature remains at the same low values (-30 °C) of impact modified nylon 6 without any polypropylene and then increases. The ductile-brittle transition temperatures of these blends are independent of the MA content (0.2 and 0.4% MA) until the point of phase inversion is reached; beyond this, blends based on PP-g-MA with 0.4% MA show a lower ductile-brittle transition temperature. The ductile-brittle transition temperatures are lower than those of blends based on unfunctionalized polypropylene (dotted line). From these data it is clear that using a maleic anhydride grafted polypropylene leads to significant improvements in the low temperature toughness of these blends.

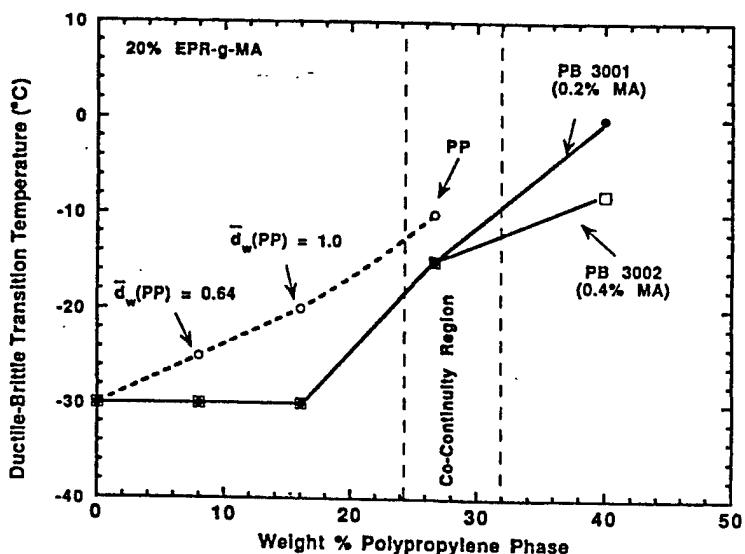


Fig. 26 Ductile-brittle transition temperature as a function of the percentage of polypropylene or maleated polypropylene in ternary blends with nylon 6 and 20% EPR-g-MA (is the weight average particle diameter).

Maleated rubbers such as EPR-g-MA and SEBS-g-MA were found to be good impact modifiers and compatibilizers for nylon 6/polypropylene blends. Both rubbers were equally effective for room temperature toughening. The ductile-brittle transition temperature of these toughened blends depends on the amount and type of rubber used and its degree of dispersion, as well as the weight fraction and degree of dispersion of the polypropylene phase. EPR-g-MA gives rise to blends with lower ductile-brittle transition temperatures than those based on SEBS-g-MA rubbers evidently because of the lower modulus of the EPR-g-MA material at low temperatures. However, SEBS-g-MA seems to be a better compatibilizer than EPR-g-MA rubbers, as judged by the degree of dispersion of polypropylene and the rubber in the blends. The lowest ductile-brittle transition temperatures for these blends are obtained when the nylon 6 is the continuous phase and the rubber and polypropylene are finely dispersed in it. The molecular weight of nylon 6 and polypropylene affect the toughness of the blends through changes in morphology in response to the melt viscosity of these components. By simply adjusting component melt viscosities nylon 6 or polypropylene can be the continuous phase. Toughness was greatest for blends where the nylon 6 phase was continuous or co-continuous and the rubber was well dispersed in it. Molecular weight also influences the intrinsic ductility of the pure components.

4. Polycarbonate-based Blends

Bisphenol A polycarbonate (PC) is widely used as an engineering material (141, 142) because of such desirable properties as optical clarity, toughness and high heat distortion temperature. However, PC has some characteristics that limit its use in many applications; for instance, its exceptional toughness is not retained in thick molded sections, in the presence of sharp notches (143-145), or at low temperatures. Improvements in these toughness deficiencies can be resolved by blending PC with appropriate rubber-containing materials.

Addition of small amounts of core-shell impact modifier particle, of the type mentioned earlier, to polycarbonate leads to reduced notch sensitivity, toughness of thick sections and good low temperature toughness with only small sacrifices in tensile behavior (143-145). We have recently examined the effects of PC molecular weight, modifier concentration and blend preparation conditions on the degree of modifier dispersion, room temperature Izod impact strength, and the ductile-brittle transition temperature (83). However, the standard notched Izod test is not an adequate method for fully characterizing the toughening effects caused by the addition of a core-shell impact modifier to PC since the thin sections (3.13 mm) and the standard notch employed do not represent sufficiently severe fracture conditions to see the true benefits and to discriminate among possible blend morphologies. Furthermore, the Izod test only gives the total fracture energy for one ligament size.

To obtain a more realistic assessment impact fracture energies were measured on PC-based materials in the form of thick specimens with a sharp notch and a varying ligament length or area (83). Typical results can be shown in Figure 27 as function of temperature for a fixed ligament length. Neat PC fails in a brittle manner in this severe test, at all temperatures used, for both high (H-PC) and medium (M-PC) molecular weight grades. Figure 27 also shows the results for blends containing 6% modifier prepared in different ways. Blends prepared in the twin screw extruder at 260°C have the highest fracture energy at room temperature and the lowest ductile-brittle temperature, 10°C for blends based on M-PC (Figure 27) and 5°C for blends based on H-PC, for all process conditions. Blends prepared in the single screw extruder based on H-PC show ductile fracture above 40°C while corresponding blends based on M-PC were brittle at all testing temperatures.

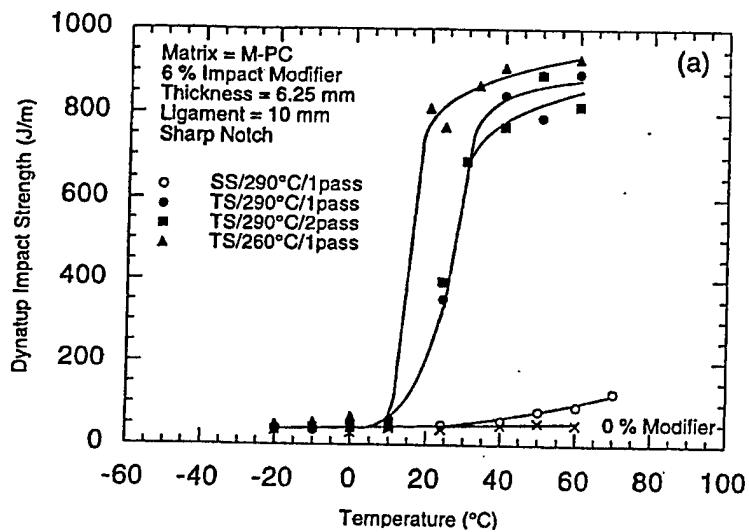


Fig. 27 Dynatup impact toughness of PC/6% modifier blends prepared by different procedures using thick specimens with a sharp notch for a medium molecular weight PC, i.e. M-PC.

A Vu-Khanh type analysis was made (83) to further examine the effects of polycarbonate molecular weight and blend compounding conditions, see Figure 28. The neat polycarbonate and blends prepared in the single screw extruder all show brittle behavior while all blends prepared in the twin screw extruder show very ductile behavior. The fracture energy at initiation for neat polycarbonate is slightly higher for the higher molecular weight grade; however, the tearing modulus is zero for both

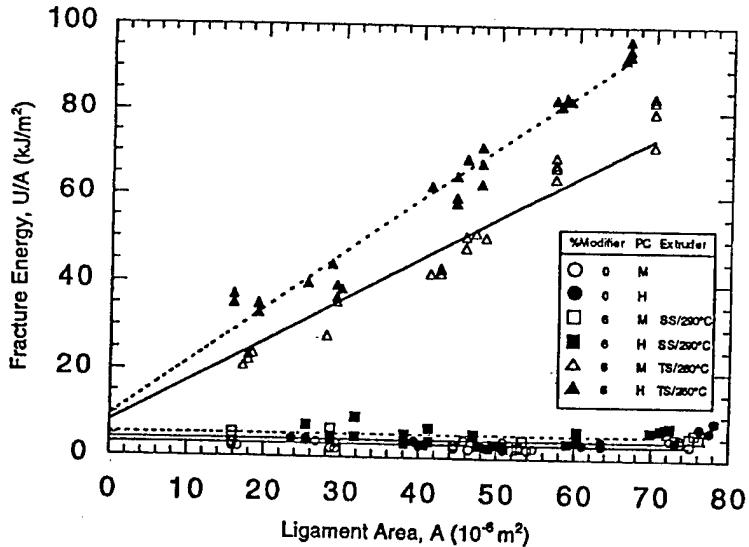


Fig. 28 Fracture energy as a function of ligament area for neat PC and PC/6% modifier blends based on M-PC and H-PC prepared by different procedures using thick specimens with a sharp notch.

grades. The values of G_i obtained for neat PC, 3.2 kJ/m^2 for M-PC and 4.1 kJ/m^2 , are similar to the value of $J_{IC} = 4.8 \text{ kJ/m}^2$ obtained by Plati and Williams using the usual measurement method (146). For both PC grades, addition of impact modifier increases the fracture energy at initiation; the effect is greater for processing procedures that improve the degree of dispersion of the modifier (83) as seen in Figure 29. The tearing modulus is even more sensitive to the degree of dispersion of the impact

modifier. Only blends prepared in the twin screw extruder show finite values of tearing modulus; blends based on H-PC show slightly higher values than those based on M-PC.

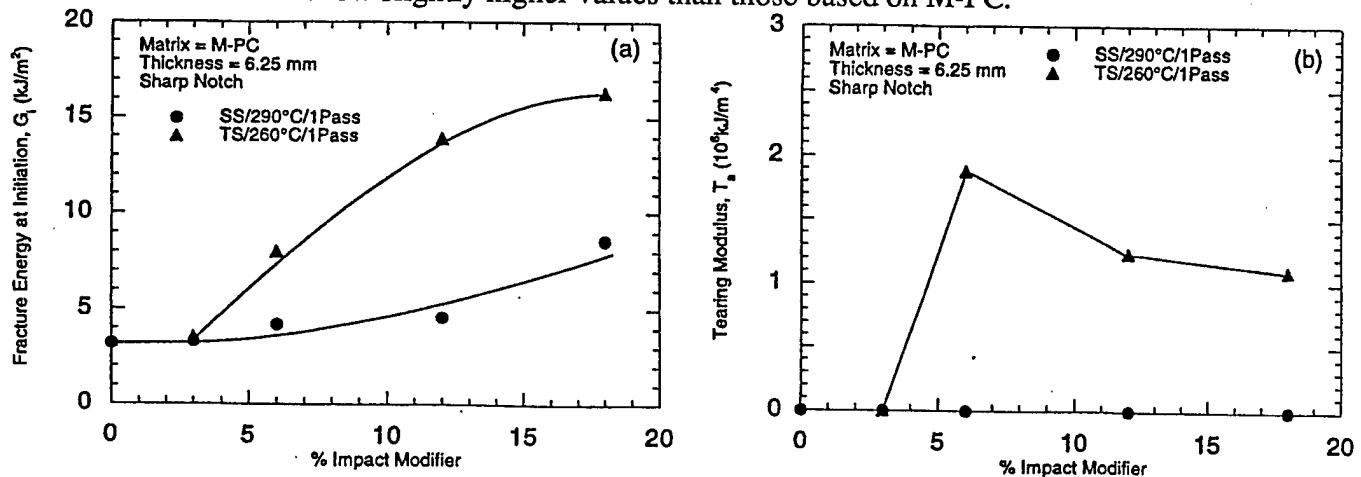


Fig. 29 Fracture energy at initiation (a) and tearing modulus (b) as a function of impact modifier concentration for M-PC blend prepared in the single and the twin screw extruder using thick specimens with a sharp notch.

Polycarbonate (PC) blends with acrylonitrile-butadiene-styrene (ABS) materials are commercially important plastics that have been found to be useful in many molding applications, particularly in the automotive industry. These blends are successful because they economically combine some of the best properties of the components, e.g., excellent impact strength (including improved notch sensitivity and thick section toughness), high heat distortion temperature, and relatively low melt viscosity for improved processibility.

There are two main types of ABS used in PC/ABS blends (28). Mass or bulk ABS is made by polymerizing styrene and acrylonitrile monomers in the presence of a dissolved butadiene-based rubber to which some grafting occurs. As the styrene-acrylonitrile (SAN) copolymer is formed, phase separation occurs followed by phase inversion, trapping some SAN within the rubber phase. The resulting rubber particles have SAN occlusions and are relatively large (0.5 to 1 μ m). The amount of rubber that can be incorporated into mass produced ABS is limited by viscosity to about 18% by weight. Emulsion produced ABS is made by a two step polymerization. First butadiene is polymerized to form a rubber; often it is a butadiene-based copolymer. Next styrene and acrylonitrile are polymerized in the presence of the butadiene-based rubber particles to produce the SAN grafted rubber and the SAN matrix. The resulting rubber particles are typically small (0.1 to 0.5 μ m), although larger particles with small SAN occlusions can be produced through variations of this process. The emulsion process can produce

ABS materials with high rubber concentrations. Often these high rubber content materials are blended with SAN or other ABS materials to achieve desired properties by varying the rubber concentration and particle size distribution.

As mentioned earlier, polycarbonate shows high notched Izod impact strength in thin sections with standard notches (notch radius = 0.25 ± 0.05 mm), but it is brittle for thicker sections (>6.2 mm) and for sharp notches (e.g., formed by a razor blade). Figure 30 shows the differences in impact strength for specimens with standard versus razor sharpened notches formed from blends of PC with two ABS materials (72). ABS 541 is a low rubber (14%), mass-produced material while ABS GRC is an emulsion-made product containing 50% rubber. Both ABS materials improve the sharp notch impact strength of PC; remarkably small quantities of the high rubber, emulsion-made ABS is required to accomplish this.

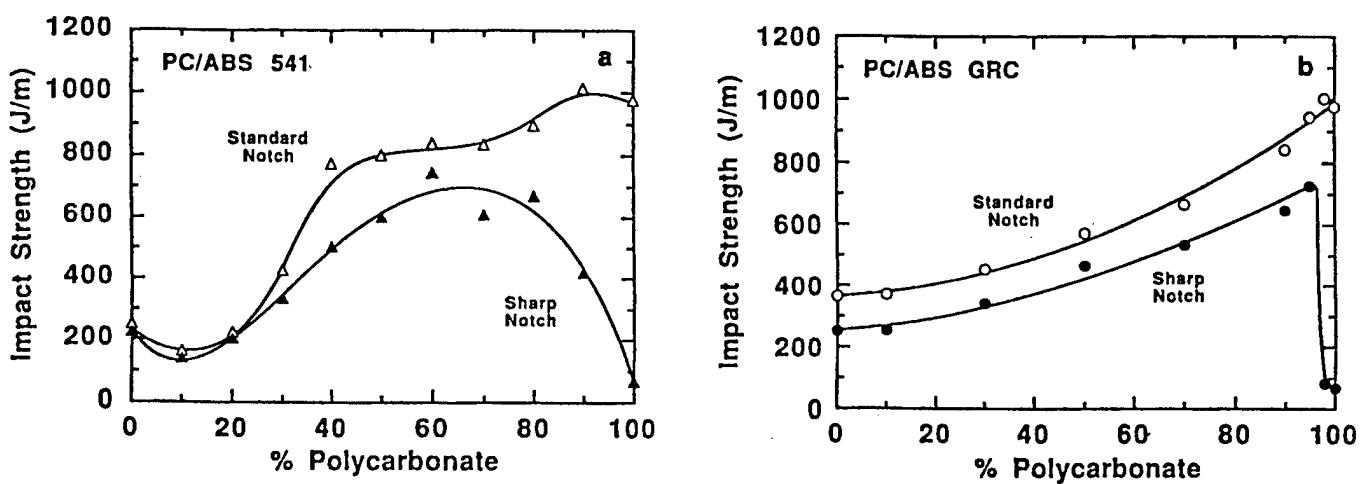


Fig. 30 Standard notch and sharp notch Izod impact strength of PC blends with ABS 541 (mass) and ABS GRC (emulsion).

The PC/ABS blends commercially used currently do not contain any compatibilizer. This is possible because the thermodynamic interaction between PC and the styrene/acrylonitrile, SAN, matrix (45) of ABS is such that adequate blends can be made (see Figure 1) under ideal circumstances. However, such blends are very sensitive to processing history since their morphology is not stabilized by any compatibilizer; morphological rearrangements that compromise performance can occur in certain kinds of molding situations. A suitable compatibilization scheme should resolve these problems and broaden the utility of such blends. Through an AASERT grant we have explored various chemical routes for this purpose and have identified one that appears quite promising. This is conceptually

illustrated in Figure 31. It begins with a special styrene/acrylonitrile/maleic anhydride terpolymer which is reacted in an extruder with 1-(2-amino ethyl) piperazine, AEP, to yield a polymer with pendant secondary amine groups. This material is being supplied to us by Allen Padwa of Monsanto (now owned by Bayer). It should be miscible with the SAN matrix of ABS. The secondary amine should rapidly react with PC (147) to give a graft copolymer as suggested in Figure 81. This scheme will be thoroughly explored as described later.

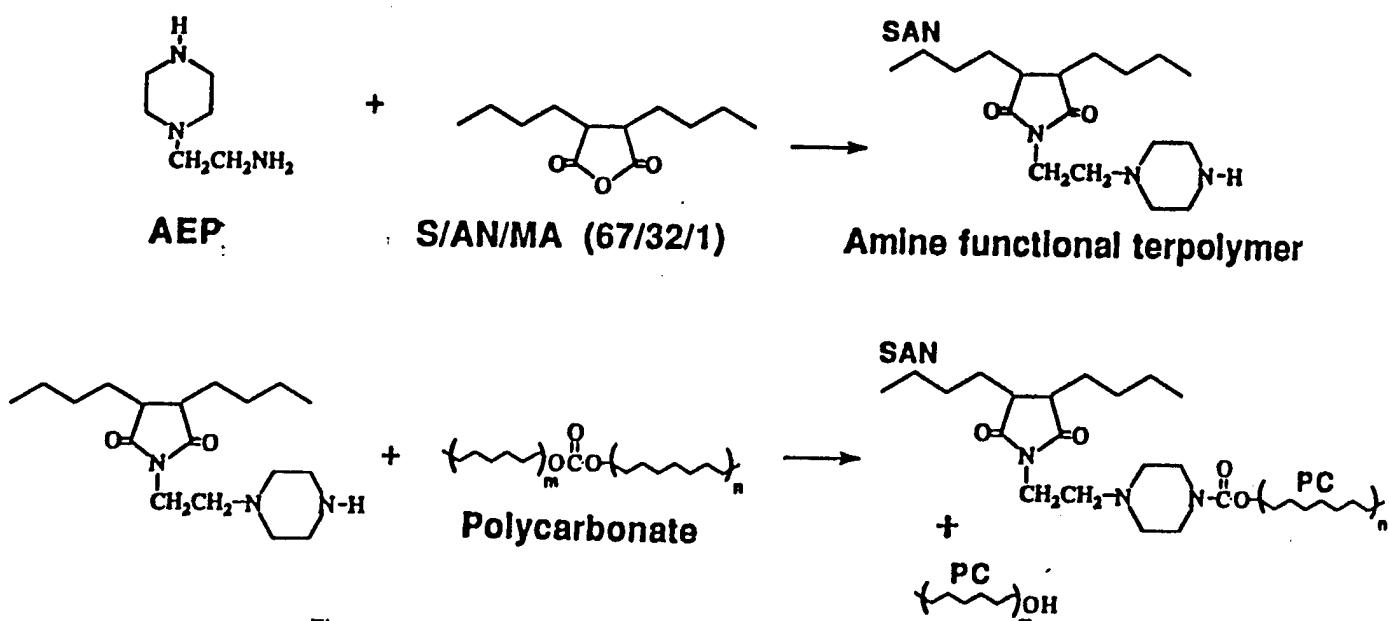


Fig. 31 Reactive compatibilization scheme for PC/ABS blends.

5. Polyester-based Blends

Poly(butylene terephthalate), PBT, is an important engineering thermoplastics that has many useful attributes, e.g. chemical or solvent resistance, without the problems associated with the high water sorption of polyamides. It is semi-ductile but fails in a brittle manner in notched impact tests. The latter problem can be solved by forming appropriate blends as shown here; however, there is relatively little information in the literature about blend strategies for PBT compared to polyamides.

Core-shell impact modifiers have proved to be more difficult to disperse in PBT than in PC. This problem can be solved if a third polymer can be found that will aid in the dispersing of the impact modifier particles in the PBT matrix (70). This additive should have greater affinity for both the shell

and the matrix than these have for each other. For some time it has been known that there is a certain amount of partial miscibility and good adhesion between PC and PBT (148-151). Recent work (152, 153) has shown that the interaction between PC and PMMA is very near the critical limit for miscibility. The fact that PMMA-based impact modifiers cannot be readily dispersed into PBT is evidence of the less favorable PMMA-PBT interaction; recall that such impact modifiers can be dispersed in PC. These interactions which can be formally expressed in terms of interfacial tensions, and classical analyses of wetting are useful (154, 155). Indeed, Dekkers and Hobbs (154) have demonstrated that in ternary blends PC tends to encapsulate PMMA domains (not core-shell particles) dispersed in a PBT matrix. Thus, it seems reasonable to propose that PC should be an effective additive for dispersing PMMA grafted rubber particles into a PBT matrix for toughening purposes.

The mechanical properties of a series of PBT blends containing 20 wt% of a commercial core-shell impact modifiers, EXL 3607, with small amounts of polycarbonate were determined. Figure 32 summarizes the Izod impact strength of specimens with both standard and sharp notches as the PC content is increased; data for the binary blend of PBT/PC without impact modifier is shown for reference. Even relatively small amounts of polycarbonate, less than 5 wt%, lead to significant toughening, and as the PC content approaches 10 wt% the blends become super tough. The specimens showed increasingly ductile fracture behavior (i.e., lateral contraction and whitening in the deformation zone) as the PC content was increased. The addition of polycarbonate does not significantly alter the modulus or yield stress until its content exceeds 10 wt%.

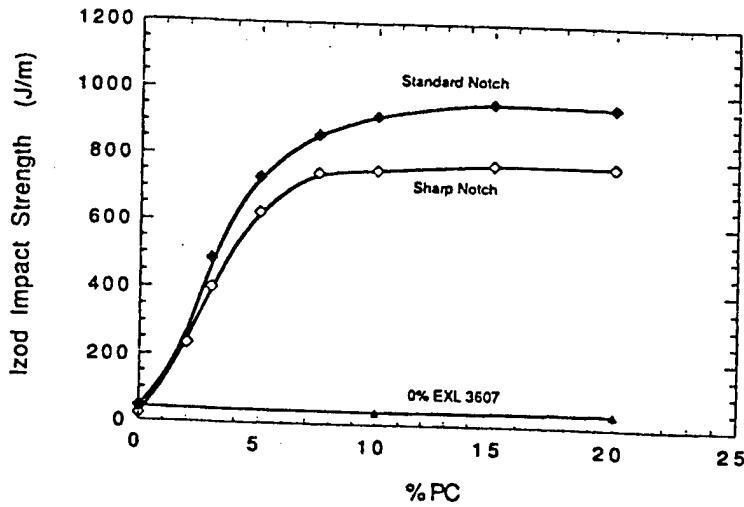


Fig. 32 Effect of PC (x wt%) content on the notched Izod impact strength of PBT (80-x wt%)/EXL 3607 blends. All blends contain 20 wt% of the commercial core-shell impact modifier.

The use of ABS materials for impact modification of PBT has been reported in the literature (87, 156-160) with widely differing results; some PBT/ABS blends are available commercially. The latter do not employ any compatibilizer, and, as a result, the properties of these blends are very dependent on processing history. The widely varying results found in the literature, based on our own experience, stem from the unstable morphology of uncompatibilized blends and a stronger sensitivity of PBT to the type of ABS used than found for PC earlier. Figure 33 illustrates the latter point by showing the impact strength versus temperature for blends of PBT with 40% of three different emulsion-made ABS materials (identified by the weight percent rubber they contain, i.e., 38, 45 and 50%). All of the blends with ABS have better toughness than pure PBT which is brittle at room temperature. However the levels of toughness seen for these blends can only be achieved using highly optimized processing conditions with little tolerance for slight variations. Rubber content of the ABS would be expected to be a key variable in blend performance; however, the ABS containing 50% rubber does not perform as well as those containing 38 and 45%; the reasons for this are not clear at the present time.

Addition of an appropriate compatibilizing agent should improve the blend performance and perhaps widen the permissible processing window. We have developed copolymers of methyl methacrylate, MMA, and glycidyl methacrylate, GMA, (plus a small amount of acrylate for thermal stability) for this purpose, see Figure 34. These copolymers are miscible with the SAN matrix of ABS (161) and react with the end groups of PBT (162). The benefits of incorporating such a compatibilizer in a blend of equal parts PBT and an ABS containing 45% rubber is shown in Figure 35. Adding 5% of a 90/10 MMA/GMA copolymer reduces the ductile-brittle transition temperature by nearly 30% relative to the control blend without compatibilizer.

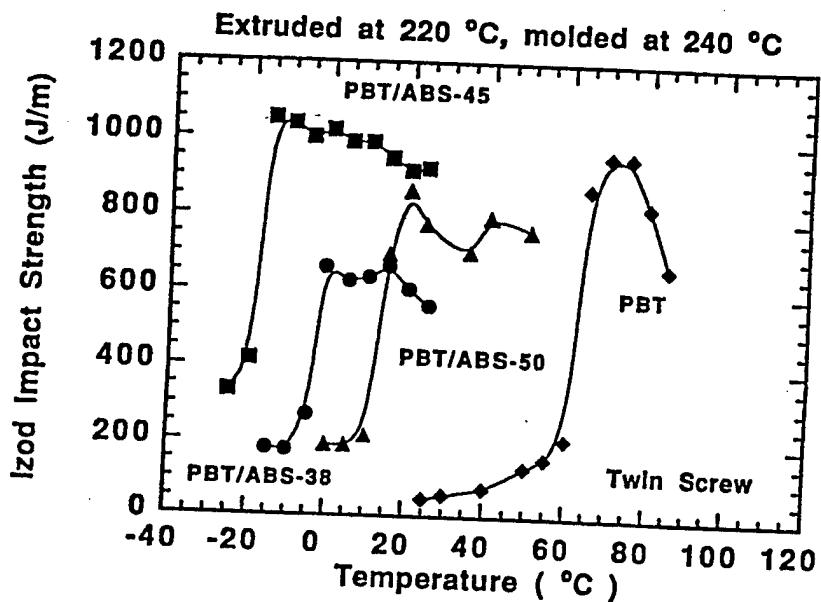


Fig. 33 Effect of temperature on notched Izod impact strength for blends containing 40 wt% ABS. The blends were prepared at 220°C in a twin screw extruder and molded at 240°C. Results for PBT shown for comparison.

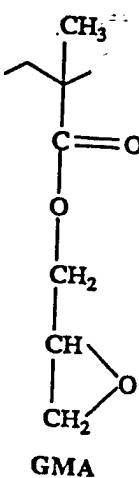
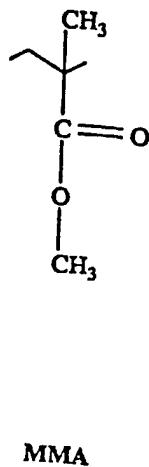


Fig. 34 Repeat units in MMA/GMA copolymers. In practice a small amounts of an acylate monomer is also incorporated to prevent depolymerization.

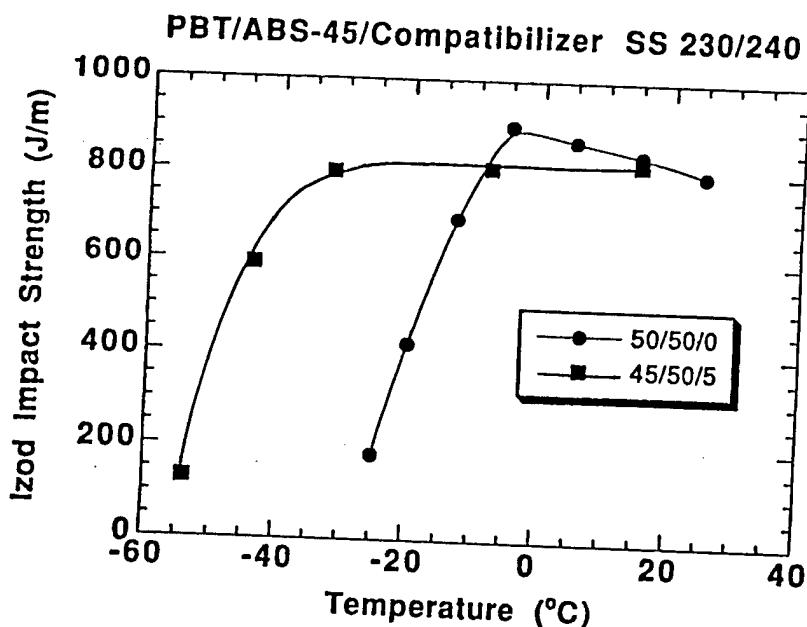


Fig. 35 Effect of MMA/GMA reactive compatibilizer on low temperature toughness of PBT/ABS blends.

IV. STATEMENT OF WORK: PROPOSED RESEARCH

The long term goal of this research program is to develop the fundamental principles needed for successfully blending or alloying immiscible polymers into materials that combine the properties or functions of the components in an advantageous manner. Of course, the only route to this general knowledge is investigation of specific systems such as those mentioned earlier and others described here. These are not simply model systems of only academic interest, but they have been carefully chosen to produce near term benefits by providing light weight, super tough formulations of both commercial and military interest. All will have value as structural materials for use in applications such as transportation systems; packaging of appliances, instruments, and computer systems; ballistic protection for the soldiers or materiel; etc. Each system to be studied consists of a rigid, semi-ductile engineering thermoplastic matrix combined with a rubber phase in some form for the purpose of producing an alloy that is super tough under severe fracture or environmental conditions. A central issue is to develop effective compatibilization strategies for each type of system that provides control and stability of the alloy morphology and adequate strength of the interface between its phases. Reactive schemes that form block or graft copolymers at the interface during processing are the strategies of choice. The systems selected and the questions we raise about these represent logical selections for the next incremental advancement towards our ultimate goal.

Many elements are involved in the rational development of high performance polymer alloys. Success in this area requires a long term program dedicated to combining state-of-the-art skills in both formulation and evaluation. On the one hand, our research involves developing new reactive compatibilization schemes that are matched with the most appropriate polymer melt processing technology. On the other hand, we continually seek more advanced methods for evaluating the chemical changes that have occurred in the blends produced, blend morphology, fracture toughness, and deformation mechanisms. The following outlines our plan for the future in more detail; the first three items deal with general concepts, techniques and approaches while the latter three describe specific systems to be explored.

1. Compatibilization and Morphology Generation

Our future work will continue to utilize the very effective amine-anhydride reaction scheme for compatibilization of blends based on polyamides. We will also develop more fully schemes involving reaction of epoxide rings with acid end groups for polyester matrices and secondary amines with carbonate linkages for polycarbonate matrices as described earlier and in item 4 below. New chemistries will be explored if necessary to accomplish our goals.

As summarized above, we have learned a great deal recently about morphology generation in reactive systems. We will continue to explore how rheological issues and processing protocols (e.g., compounding in a twin screw extruder followed by injection molding) interact with the chemistry occurring to affect morphology generation and stability in the blend systems identified below. Cryogenic microtomy, selective straining, transmission electron microscopy, and image analysis are standard tools in our laboratory for evaluating blend morphology. However, additional tools for morphology characterization would be very useful for our program. To this end, we plan to initiate a collaboration with Dr. Nora Beck Tan of the Army Research Labs to examine the feasibility of using small angle x-ray scattering, SAXS, for this purpose. Dr. Tan has the facilities and expertise for such measurements and has expressed her interest in this collaboration.

2. Fracture Characterization

The term "super tough" has not been defined precisely in the field of plastics, but the term generally refers materials having Izod impact strengths equal to or greater than 800 Joules/meter (or 15 ft lb/in) presumably measured at room temperature on thin specimens (1/8 inch thick) with a standard notch (radius = 0.010 inch). The latter conditions usually approximate a condition of plane stress in the test specimen and does not give a realistic assessment of material performance in more demanding fracture situations involving plane strain conditions that prevail in thicker specimens or when there is a sharp notch or crack. Furthermore, the Izod test is only a single point measurement with regard to ligament size and does not allow differentiation between the energy needed for initiation, versus

propagating the fracture process. In nearly all applications, fracture behavior at low ambient temperatures (e.g. cold weather) is an issue of major importance.

In view of the issues mentioned above, it is important to use more sophisticated and extensive means for characterizing toughness of the materials generated in this program (see following sub-sections). Thus, we will measure the fracture energy, U , as a function of ligament area varying the specimen thickness and the notch geometry. The data will be analyzed in terms of the Vu-Khanh approach (125) described above, to obtain the parameters G_i = fracture energy at initiation and T_a = tearing modulus, or the essential work analysis of Mai, Williams, et al (135-137). We plan to obtain an in-depth experimental characterization of the fracture toughness of selected series of materials in this way and to develop a better understanding of the parameters deduced from analysis of such data. Specifically; we will explore the effect of test details (specimen thickness, notch geometry, test temperature) and material characteristics (matrix molecular weight, blend morphology, rubber phase properties, etc.) on these fracture parameters. The hope is to develop more realistic ways of characterizing super tough materials, to establish broad correlations/understanding of how blend structure and component characteristics influence the fracture parameters, and to understand how fracture parameters relate to end-use performance.

3. Toughening Mechanisms and Deformation Modes

Sub-sections 1 and 2 above address issues of formulation and fracture characterization of the specific materials systems (see sub-sections 4-6) that we propose to examine. It is also imperative to understand more about the mechanisms of toughening and the modes of deformation that are operative in each system and situation in order to generalize the knowledge base in this area. An important issue is to understand in fundamental terms the morphological limits for achieving super tough behavior, see schematic in Figure 2 and data in Figure 6 for nylon 6-rubber blends. We plan to give a high priority to these areas in our future work.

Our primary tools will be ones described in several recent publications from our program (69, 77, 83, 86) involving post-mortem analysis by transmission electron microscopy of thin sections excised

from specimens in the vicinity of an arrested crack; we have developed techniques for stopping crack growth during high speed impact testing. Such analyses allow one to follow the sequence of events within the material as they occur in the fracture process. A particularly fruitful area that we plan to explore is evaluation of the propensity of rubber particles to undergo cavitation and how this affects the toughening response. Specifically, we are interested in how rubber particle size and size distribution, in addition to rubber phase properties like modulus, crosslink density, microdomain structure, etc., affect cavitation and subsequently toughness. We will try to achieve a better understanding of what factors govern the size of the deformed zone, see Figure 20, since this seems to be key to achieving high levels of toughness.

4. ABS Containing Blends

As suggested earlier there are a wide variety of possible ABS materials and some can be very effective and economical toughening agents, if selected properly, for many engineering thermoplastics. A substantial part of our future work will be devoted to developing blends (matrix = polyamides, polycarbonate, poly(butylene terephthalate), etc.) containing ABS materials. With the help of Dr. H. Keskkula our laboratory has developed a unique expertise in ABS materials and we have gained access to a wide selection of commercial and experimental ABS materials (many are concentrates which are intermediate products not normally sold) from a spectrum of companies around the world who are interested in working with us. These materials differ in rubber content, rubber particle size and morphology, extent of grafting of styrene-acrylonitrile copolymer, SAN, to the rubber, acrylonitrile content of the SAN phase, etc which provides a rich opportunity for developing highly optimized alloys and for understanding the effects of key variables on morphology generation and toughening. Our work in this area will be in three parts.

One will use nylon 6 as the matrix; the type can be varied widely as seen above. Some years ago we did preliminary work on nylon 6/ABS blends primarily to develop compatibilization schemes (65, 67, 71, 73). We now have available to us the imidized acrylic materials used previously (71) as well as a styrene/acrylonitrile/maleic anhydride terpolymer from industrial sources as well as the MMA/GMA

materials described earlier from our own laboratory. The main focus of our work will be to explore relationships between the content and type of ABS and the compatibilizer on fracture toughness and the mechanism of toughening. We wish to expand the limits of performance currently known for this important class of commercial blends using our access to these unique materials and the techniques described earlier.

Another will use polycarbonate as the matrix. PC/ABS blends are already important commercial materials; however, they suffer some limitations that we believe we can eliminate to arrive at a more versatile second generation product. Current commercial PC/ABS blends do not contain any compatibilizer since the SAN-PC interaction is adequate enough (see Figure 1) to make usable products. However, the morphology of these alloys is unstable and can change in very deleterious ways during some types of melt processing operations; low shear conditions lead to ABS domain coalescence and loss of toughness. We have developed a compatibilization scheme for this system (see Figure 31) that we believe should solve this problem. We will aggressively pursue the evaluation of this option. We will also do a thorough characterization of the fracture behavior, toughening mechanisms, and morphology stability with and without compatibilization using a well selected array of ABS materials.

The final system uses PBT as the matrix. Again, commercial PBT/ABS blends are available that employ no compatibilizer. We feel that the MMA/GMA compatibilizer described earlier (see Figure 34 and 35) should be aggressively pursued in a manner similar to that outlined for PC/ABS above.

We believe that our work with ABS-based blends represent exciting opportunity and that we are in a unique position to make valuable practical and fundamental contributions in each of these areas. The following two items represent more high-risk areas that we intend to explore as part of this research; the initial efforts will be strictly of an exploratory nature. If promising results are found, we will seek other funds to more aggressively explore them.

5. High Modulus Super Tough Alloys

Nylon 6 blends with maleated elastomers, e.g., EPR-g-MA or SEBS-g-MA, lead to super tough materials as shown earlier. The addition of such rubber phases naturally leads to loss of stiffness relative

to neat nylon 6. Addition of a rigid phase to such blends can improve the stiffness, but can this be done in a way that does not overly sacrifice the gain in toughness caused by the rubber phase. Some very rigid polymers like SAN can undergo shear yielding when properly incorporated into a ductile matrix, like nylon 6, as shown in the literature (163) and recently demonstrated in our laboratory. There is some evidence that if the rigid phase particles are small enough that toughness can be maintained (164). Thus, we intend to explore matrices with two dispersed phases; one that is soft for toughening and one that is high modulus for achieving higher levels of stiffness than currently available in super tough materials. Inorganic fillers or fibers would be an extreme case.

6. Transparent Super Tough Alloys

Toughening by adding a rubber phase generally leads to opaqueness owing to the light scattered from this dispersed phase. However, there are enormous military and civilian opportunities for super tough materials that are also transparent. The lack of such materials is testimony to the challenge of achieving these nearly orthogonal goals; however, we intend to explore the possibilities. The obvious strategy is to use refractive index matching of the matrix and rubber phase since this can, in the limit, eliminate scattering of light by the internal interfaces. Polycarbonate is the obvious choice for a matrix since it is transparent and is super tough except under conditions of plane strain (thick sections or sharp notches). The problem is that all elastomers known to us have substantially lower refractive indices than that of PC, i.e., 1.586. Our approach will be to look for a rigid polymer with a much higher refractive index than PC that can be combined with a low refractive index elastomer in some form (core-shell particles, block copolymers, blends, random copolymer, etc.) such that very fine particles, having an "effective" refractive index similar to that of PC, can be dispersed in the PC matrix to produce toughening without scattering light. Based on information in the literature and from our recent research, there appear to be some possibilities worthy of an exploratory effort.

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III. PUBLICATIONS COMPLETED TO DATE

A. Ph.D. Dissertations:

Name		Title
Oshinski, Alan	Ph.D.	Rubber Toughening of Polyamides Using Functionalized Block Copolymers
Gonzalez-Montiel, Alfonso	Ph.D.	Reactive Compatibilization and Toughening of Nylon 6/Polypropylene Blends
Lu, Mengshi	Ph.D.	Use of Reactive Compatibilizers for Toughening Polyamides with Various Impact Modifiers
Hale, Wesley Ph.D.		Reactive Compatibilization of PBT/ABS Blends by Methyl Methacrylate, Glycidyl Methacrylate, Ethyl Acrylate Terpolymers
Wildes, Gregg	Ph.D.	Effect of Reactive Compatibilizers on the Morphology and Physical Properties of Bisphenol-A-Polycarbonate/Acrylonitrile-Butadiene-Styrene Blends

B. Paper in Print

D.R. Paul and H. Keskkula, "Toughening Agents for Engineering Polymers" Ch. 5 in "Rubber Toughened Engineering Plastics," A. A. Collyer, Ed., Elsevier Applied Sciences Publisher, Chapman & Hall, London (1994).

D.R. Paul, B. Majumdar and H. Keskkula, "Morphology of Nylon 6/ABS Blends Compatibilized by a Styrene/Maleic Anhydride Copolymer," *Polymer*, 35, 3164 (1994).

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C. Papers Submitted or Accepted for Publication

G.S. Wiles, T. Harada, H. Keskkula, D.R. Paul, V. Janarthanan and A.R. Padwa, "Synthesis and Characterization of an Amine Functional SAN for the Compatibilization of PC/ABS Blends."

W. Hale, H. Keskkula, and D.R. Paul, "Fracture Behavior of PBT/ABS Blends Compatibilized by Methyl Methacrylate-Glycidyl Methacrylate-Ethyl Acrylate Terpolymers."

W.R. Hale, L.A. Pessan, H. Keskkula and D.R. Paul, "Effect of Compatibilization and ABS Type on Properties of PBT/ABS Blends."

W. Hale, H. Keskkula, and D.R. Paul, "Effect of Crosslinking Reactions and Order of Mixing on Properties of Compatibilized PBT/ABS Blends."

R.A. Kudva, H. Keskkula and D.R. Paul, "Morphology and Mechanical Properties of Compatibilized Nylon 6/Polyethylene Blends."

T. Harada, E. Carone, Jr., R.A. Kudva, H. Keskkula, and D.R. Paul, "Effect of Adding an Imidized Acrylic Polymer to Super Tough Nylon 6 on Stiffness and Toughness."

W. Hale, J-H. Lee, H. Keskkula and D.R. Paul, "Effect of PBT Melt Viscosity on the Morphology and Mechanical Properties of Compatibilized and Uncompatibilized blends with ABS."

O. Okada, H. Keskkula, and D.R. Paul, "Nylon 6 as a Modifier for Maleated Ethylene-Propylene Elastomers,"

IV. PARTICIPATING SCIENTIFIC PERSONNEL

<u>NAME</u>	<u>STATUS</u>	<u>COMMENTS</u>
D.R. Paul	Faculty	Summer support
H. Keskkula	Research fellow	Partial support
M. Lu	Ph.D. student	Ph.D. granted
A.J. Brady	M.S. Candidate	Did not graduate
G.S. Wildes	Ph.D. student	Ph.D. granted
W.R. Hale	Ph.D. student	Ph.D. granted
A.J. Oshinski*	Ph.D. student	Ph.D. granted
A. Gonzalez-Montiel	Ph.D. student	Ph.D. granted

R.A. Kudva	Ph.D. student	Continuing
E. Hage*	Visiting Scholar	Completed
Y. Kayano*	Visiting Scholar	Completed
N. Kitayama*	Visiting Scholar	Continuing
O. Okada*	Visiting Scholar	Completed
M. Laura	Ph.D. student	Continuing
T. Harada*	Visiting Scholar	Completed
J. Lee*	Visiting Scholar	Completed

*No salary provided by this contract

V. Report of Inventions and Subcontracts

None. See Form 882